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ABSTRACT

Chemical oceanography or marine chemistry are taught in many colleges and universities. This publication provides sources for instructors of such courses. The first section of this report is a detailed composite outline of a course in chemical oceanography. It includes fundamental topics taught in many chemical oceanography classes. The outline also serves as a guide to the problem and reference sections in the report. Following the course outline are 56 pages of problems and 25 pages of bibliographical references. Problem topics include the physical chemistry of sea water, ocean models, and ocean pollution as well as nearly every other major topic in the marine chemistry field. (RH)

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A Source Book for Teaching

CHEMICAL OCEANOGRAPHY

Theodore C. Loder

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January, 1977

Report # UNH-SG-AB-102

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TABLE OF CONTENTS

Introduction. 1

List of Contributors. 5

Suggested Course Outline. 7

Problems. 11

A. Physical and Thermodynamic Properties of Water. 11

1. Thermodynamics and chemistry 11

2. Water structure. 17

3. Physical processes of the ocean. 21

B. Composition and General Nature of Seawater. 29

1. Salinity 29

2. Major and minor ions 33

3. Trace elements 47

4. Residence times. 47

C. Gases 57

1. Atmosphere and exchange processes. 57

2. Non-carbon dioxide gases 61

a. Analytical methods. 61

b. Distribution and concentration. 63

3. Carbon dioxide and related principles. 71

a. pH, alkalinity. 71

b. Carbon dioxide equilibrium and distribution 77

c. Carbonates. 81

D. Nutrients 87

1. Analytical methods 87

2. Distributions and relationships. 87

E. Organic Matter in Seawater. 95

F. Productivity. 99
G. Geochemical Cycling 103
1. Silicate and clay equilibrium. 103
2. Geochemical problems and sediments 105
H. Models. 113
I. Isotopes, Radioactive and Stable. 117
J. Pollution of the Sea. 121
Course Reference Lists. 125
A. Introduction - General Reference Books. 125
B. Physical and Thermodynamic Properties of Water and Sea Water. 126
C. Composition and General Nature of Sea Water 128
1. Salinity - Definitions, measurements and variations. . . 128
2. Major and minor ions in sea water. 128
3. Origin of seawater 129
D. Physical Processes of the Ocean 130
E. Dissolved Gases in Sea Water. 131
1. Non-carbon dioxide 131
a. Distribution and solubility 131
b. Analytical methods. 132
c. Exchange processes across sea surface; equilibrium. 132
d. Anoxic conditions and redox potential 133
2. Carbon dioxide 134
a. pH, alkalinity. 134
b. Carbon dioxide - alkalinity relationships 135
c. Analytical methods. 136
d. Exchange between the sea and the atmosphere 136
e. Carbonates. 137

f. World distribution of CO_2 138
F. Geochemical Cycling 138
G. Nutrients 139
1. Nitrogen 139
a. Analytical methods. 139
b. Variation and distribution of nitrogen in the sea . 139
2. Phosphorus 140
a. Analytical methods. 140
b. Variation and distribution of phosphorus in the sea. 140
3. Silicon. 141
a. Sources and silica mass balance 141
b. Analytical methods. 142
c. Biological importance 142
d. Distribution of silicon in the sea. 142
H. Organic Matter in the Sea 142
1. Dissolved organic matter 142
a. Origin and fate 142
b. Distribution and complications. 143
2. Particulate organic matter 143
a. Origin and composition. 143
b. Surface films 144
3. Biological effects on seawater chemistry 144
I. Marine Sediments. 145
J. Chemical Models of the Oceans 147
K. Minor Elements and Trace Metals 147
L. Radioisotopes and Stable Isotopes 148
M. Pollution of the Sea. 148

INTRODUCTION

The study of chemical oceanography has grown tremendously over the past few years. Certainly a major part of this growth has been concerned with the various aspects of the chemistry of pollution as governments attempt to reduce the amount of marine pollution. However, pollution problems are only a part of chemical oceanography and a solid foundation in chemistry and chemical processes in marine waters is a necessary prerequisite to understanding many oceanographic problems.

Chemical oceanography or marine chemistry courses are taught in many colleges and universities today, and range from undergraduate to advanced graduate courses. As more colleges attempt to offer courses in these areas, chemistry, biology and earth science faculty find themselves teaching in an area where they may have had only limited experience. This report should be a useful source of information for these people. It should also be useful for those who have taught for a short while and are still learning and trying new areas and ideas. For those who have taught a long time (and perhaps have gotten into a teaching-material rut) it should provide new information to be incorporated the next time chemical oceanography is taught.

The concept of this report originated at an informal session on the teaching of chemical oceanography at a Chemical Oceanography Gordon Research Conference in Santa Barbara, California. Later we solicited course outlines, problem sets, exams and reference lists from scientists teaching both introductory and specialized advanced courses in the field. The materials were compiled into this source book. The contributors are listed on page 5.

The first section of this report is a detailed composite outline of a course in chemical oceanography. It includes the fundamental topics that are taught in most chemical oceanography courses today. The emphasis on any given topic varies from course to course depending on the instructor's interests and time constraints. This outline also serves as a guide to the problem and reference sections in the report.

The second section includes examination and homework problems. We eliminated test questions that were obvious such as "define salinity" and retained those we thought could be used by others. Some questions are rather straightforward while others are inventive, original, humorous and downright fun. All, we hope, will challenge the student or teacher while teaching a useful fact, principle or method.

The problems have been edited slightly to fit the format of this report but the contents remain essentially as we received them from the many contributors. We did not, during our editing process, work each problem and, therefore, claim no responsibility for their workability or their answers. If you are losing sleep over the method or answer to a problem, write us for ideas or, better yet, write the person who assigned the problem to their misfortunate students. The name of each contributor is given at the end of each problem, although the named contributor may not be the original source of the problem. The problems were printed in reduced form to minimize printing costs. Blank pages have been left in the text to allow space for notes.

The third section is a series of reading lists for the various major topics in chemical oceanography. The lists are not intended to be complete but should provide a good source of major references for background reading in the areas listed and provide an idea of what other teachers feel are the important articles. We have included primarily current citations.

We have not included a section on laboratory exercises because most of those given only included the analysis of the usual sea water chemical parameters, such as salinity, dissolved oxygen, alkalinity, pH and nutrients. Since these methods are adequately referenced, we do not feel it necessary to repeat them here. Depending on the course level, many teachers try to include a field experience as part of the lab.

We would like to thank the contributors for their efforts, for without their time in bringing material together and sending it to us we could not have completed this source book.

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Durham, New Hampshire
January, 1977

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SUGGESTED COURSE OUTLINE

I. Introduction

A. What is chemical oceanography

B. Introduction to literature

C. Historical perspective - Marcet, Dittmar, etc.

II. Physical and thermodynamic properties of water

A. Selective review of thermodynamics

1. Thermodynamic parameters: energy, work, heat, and entropy

2. Activity and chemical potential

3. Activity coefficients

4. Ionic strength

B. Structure of water

1. Structure of ice

2. Models for water structure

3. Thermal anomalies

4. Effect of temperature and pressure on water structure

III. Composition and general nature of sea water

A. Effect of adding ions to water - ionic potentials, structure makers and breakers

B. Salinity - definitions and measurements

C. Variation of properties with salinity

D. Major and minor ions in sea water - distribution and complexes

E. Resident times

F. Origin of sea water

IV. Physical processes of the ocean

A. Currents and water masses

B. Bubbles and other atmospheric processes

V. Dissolved gases in sea water

A. Non-carbon dioxide

1. Distribution and solubility

2. Analytical methods

3. Exchange across sea surface; equilibrium

4. Anoxic conditions and redox potential

B. Carbon dioxide

1. pH, alkalinity

2. Carbon dioxide - alkalinity relationships

3. Analytical methods

4. Exchange between the sea and the atmosphere

5. Carbonates

6. World distribution of CO_2

VI. Geochemical Cycling

A. Silicate equilibrium models (Sillén)

B. Elemental mass balance budgets

VII. Nutrients

A. Nitrogen

1. Analytical methods

2. Nitrogen cycle in the sea

3. Nitrogen fixation

a. Assimilation of fixed nitrogen

b. Regeneration of NO_3^-

4. Variation and distribution of nitrogen in the sea

B. Phosphorus

1. Forms: organic P, particulate P
2. Analytical methods
3. Phosphorus cycle in the sea
4. Distribution of Phosphorus in the sea

C. Silicon

1. Sources and silica mass balance problem
2. Analytical methods
3. Biological importance
4. Distribution of Silicon in the sea

VIII. Organic matter in the sea

A. Dissolved and particulate organic matter

1. Origin and composition
2. Analytical methods
3. Distribution and complications
4. Dissolved and particulate relationships
5. C:N:H relationships
6. Surface films

B. Biological effects on seawater chemistry

1. Productivity
2. Analytical methods: C^{14}, light-dark bottle technique
3. Chlorophyll
4. Seasonal cycles

IX. Suspended particulate matter and ocean sediments

A. Composition and distribution

B. Input to world's oceans

C. Chemistry of sediment and sea-water interactions

X. Chemical models of the oceans

A. Ocean circulation

B. Chemical processes affected by circulation

C. Discontinuous models (Box models)

D. Continuous models (one-dimensional advection-diffusion)

XI. Minor elements and trace metals

A. Redox reactions in seawater

B. Metal complexes in seawater

C. Manganese nodules

D. Distribution in world ocean

XII. Radioisotopes and stable isotopes

A. Stable isotopes

B. Radioisotopes

1. natural radionuclides

2. fall out nuclides

C. Isotopic dating

D. Use in water mass identification and dating

XIII. Pollution of the sea

PROBLEMS

A. *Physical and Thermodynamic Properties of Water*

1. *Thermodynamics and chemistry*

1. We may consider three ways in which a chemical equilibrium in a complex medium such as seawater can be characterized. These three approaches use thermodynamic equilibrium constants, K, (defined in terms of activities), stoichiometric equilibrium constants, K*, and apparent equilibrium constants, K'.
   (a) Derive an expression which shows the relationship between K' and K* for the second dissociation of carbonic acid in seawater.
   (b) Considering the relationship between K* and K and in view of the thermodynamic expressions for the variation in K with temperature and pressure what conclusions can one reach about the general behavior of K* and K' with T and P? (Kester)

2. Calculate the activity coefficient of a solution whose Na^+ activity is 0.7 M and whose stoichiometric concentration is 2.0 M. (Duedall)

3. Derive an expression relating the apparent solubility product, K'_{sp}, of a solid M_mN_n to the thermodynamic K_{sp} in terms of free activity coefficients and stoichiometric association constants for ion-pairs formed by M and N in a medium containing cations C_j and anions A_i. (Kester)

4. If, for the calcium phosphate mineral apatite, $pK'_{sp} = 30$, would the following seawater be over-, under-, or just saturated? The seawater has the following properties: $(Ca) = 0.01$ M, $(PO_4^{-3}) = 3 \times 10^{-6}$ M, pH = 8.0. Use as the formula for apatite: $Ca_5(PO_4)_3OH$. What are the sources of error in extending this type of calculation to the oceans? (Gordon)

5. Assume the K_{sp}, the thermodynamic solubility product, for the mineral brucite ($Mg(OH)_2$) is 7.08×10^{-12} and $\gamma = 1$. Assume a reasonable value for $\gamma_{Mg^{2+}}$ and use the following mass action law--$K_{sp} = (a_{Mg^{2+}})(OH^-)^2$--to calculate the stoichiometric concentration of Mg^{2+} in a solution of seawater of salinity 35 °/oo. (Hint: remember from your freshman chemistry that pH + pOH = 14.) (Duedall)

6. Illustrate with equations pertinent to the marine environment how thermodynamics can be used for predicting chemical events. (Baier)

7. Which is stable at T = 298.15°K, P = 1 atm in nearly pure water, MnO or $Mn(OH)_2$? (Morse)

8. Given for NaCl: $S_{25°} = 17.3$ cal/deg-mole, $C_p = 10.98 + (3.90 \times 10^{-3}T(°K))$, $\rho = 2.16$ g/cm^3, $\alpha = 1.26 \times 10^{-4}$ deg^{-1}(20-200C), $\beta = 4.26 \times 10^{-6}$ atm^{-1}. Calculate S at 100 atm 200C. (Morse)

9. In the system solid NaCl, ice, solution, vapor, describe the events which occur in terms of the phase rule as heat is added to the system (assume H_2O >> NaCl). (Hammond)

10. The following is a chemical analysis of a natural water:

Species	ppm	Species	ppm	Species	ppm
HCO_3^-	164.7	Ca^{+2}	50.1	Ba^{+2}	0.19
SO_4^{-2}	8.1	Na^+	5.4	SiO_2	12.1
Cl^-	4.0				

(a) What is ionic strength?

(b) What are activity coefficients and activities assuming no complexing?

(c) Assuming ion pair formation only between Ca^{+2} and SO_4^{-2} (to form $CaSO_4^o$), what is the activity of SO_4^{-2} after correction for complexing?

(d) Assuming no complexing with barium, is the water supersaturated with respect to barite?

(e) What is wrong with the analysis (prove)?

$\Delta G^o_{fBa^{+2}} = -134.0$ $\Delta G^o_{fCa^{+2}} = -132.18$ $\Delta G^o_{fSO_4^{--}} = -177.34$

$\Delta G^o_{fBaSO_4} = -323.4$ $\Delta G^o_{fCaSO_4^o} = -312.67$ (Morse)

11. One group of radiolarians, the Acantharia, make their skeletons out of $SrSO_4$. The K_{sp} for the reaction $SrSO_4 \rightleftharpoons Sr^{2+} + SO_4^{2-}$ is 3.2×10^{-7} at 25C and 1 atm. Typical total concentrations of Sr and SO_4 in seawater are 9.1×10^{-5} and 0.028 moles/l respectively. Calculate whether these $SrSO_4$ skeletons should dissolve in surface seawaters at 25C. State your choice of activity coefficients and whether their uncertainty would make a difference in your conclusion. Given the following data, calculate K_{sp} at 5000 meters and 0C and decide whether the $SrSO_4$ skeletons will be more soluble or less in deep waters.

	ΔH^o, kcal/mole	ΔV^o, cc/mole
$SrSO_4$	-345.3	46
Sr^{2+} aq.	-130.4	-18
SO_4^{2-} aq.	-216.9	22

Will the uncertainty introduced by assuming γ's, ΔH's and ΔV's are not P or T dependent make any difference in your final conclusions in this case? If the O^{18}/O^{16} ratio were used to develop a temperature scale for $SrSO_4$ skeletons (like that established for $CaCO_3$), what steps should be taken to set up a reliable scale? What problems and assumptions would be most serious? (Baier)

12. Consider the dissociation of HA (a weak acid) in seawater. Calculate the fractions α_0 (which you will remember is HA/C_t) and α_1 (which is A/C_t) in seawater. Use $pK_{HA} = 12$. (Duedall)

13. Demonstrate the difference between molarity and molality for a constituent in seawater. Use, if you wish, the concentration of Mg in seawater whose concentration is 1.297 °/oo (wt/wt). [Mol. Wt. = 24.312 g]. (Duedall)

14. Explain why the activity coefficients for Na_2SO_4 and $MgSO_4$ are considerably less than those of the other salts. (Duedall)

15. Describe (mathematically) what is meant by an equation of state; use density as the state variable. (Please don't give the Knudsen equation.) (Duedall)

16. For sugar, the freezing point depression is $T_o - T = C_f m$, where m = molarity and C_f is constant for sugar which does not dissociate.

(a) Calculate the freezing point depression for 0.5 m NaCl, 0.5 m Na_2SO_4, and 0.5 m $MgSO_4$.

(b) Explain how you think C_f is affected by ion-pairing in seawater. Give some examples. (Duedall)

17. Absorption of energy from a pressure jump occurs primarily at which step in the magnesium sulfate association? $(Mg^{2+})(SO_4^{2-}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Mg^{2+})H_2O(SO_4^{2-}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (Mg^{2+})(H_2O)_2(SO_4^{2-})$

1. k_1 2. k_{-1} 3. k_2 4. k_{-2} 5. none (Mathewson)

18. In many calculations, we assume activity coefficients are unity for the sake of simplicity. Rigorously, we should use a definition such as pH = - log $[H^+]_{\gamma_H}$, and the equilibrium expression for the ion product of water: $[H^+][OH^-]\gamma_H\gamma_{OH} = K_w^o N_w^o$, where $K_w^o = 1.0 \times 10^{-14}$ at 25C, and N_w is the mole fraction of water in the solution. A much less stringent approximation is that the activity coefficients of all univalent ions are the same function of the ionic strength ($\gamma_H = \gamma_{OH}$). Show that under this approximation, the addition of the salt of a strong acid and a strong base to pure water does not affect the pH by more than 0.01 units until the concentration of salt reaches values of the order of 1 mole/liter. (Butler)

19. For each equation listed below place a mark in the appropriate column for each subject where the reaction represented is important. (Gordon)

	Magnitudes of physical properties of seawater	Mineral extraction processes	Decay of organic matter	Desalination of seawater	Geologic control of seawater pH
(a) $Ca^{2+} + CO_3^{2-} = \underline{CaCO_3}$					
(b) $Mg^{2+} + SO_4^{2-} = MgSO_4^o$					
(c) $(CH_2O)_{106} \cdot (NH_3)_{16} \cdot H_3PO_4 + 138\ O_2 =$ $106\ CO_2 + 16HNO_3 + H_3PO_4 + 122\ H_2O$					
(d) $Ca^{2+} + CO_3^{2-} = CaCO_3^o$					
(e) $\underline{NaCl} \overset{H_2O}{\rightleftharpoons} Na^+ + Cl^-$					
(f) $H_2O(\ell) + \text{heat} = H_2O(g)$					
(g) $2HCO_3^- = H_2CO_3 + CO_3^{2-}$					
(h) $Ca^{2+} + SO_4^{2-} = \underline{CaSO_4}$					
(i) Mica + H^+ + water = kaolinite + K^+					
(j) $Cl_2 + 2Br^- = Br_2 + 2Cl^-$					

20. Which of the following reactions would you expect to be the fastest? the slowest?

1. $NaOH + HCl \rightleftharpoons NaCl + H_2O$ 2. $Ca(OH)_2 + HCO_3^- \rightleftharpoons CaCO_3 + H_2O + OH^-$

3. $O_2(g) + 4H^+ + 4e \rightleftharpoons 2H_2O$

State briefly the utility of a thermodynamic evaluation of a system in the ocean where equilibrium is essentially nonexistent.

List 5 possible errors inherent in measurements of E_H. How is E_H related to pE?

Draw a pE - pH diagram for seawater using the following thermodynamic data at 25C. Label all lines defined by these equilibria.

	log K
$H^+ + e \rightleftharpoons 1/2\ H_2\ (g)$	0
$1/4\ O_2\ (g) + H^+ + e \rightleftharpoons 1/2\ H_2O$	20.75
$1/2\ NO_3^- + H^+ + e \rightleftharpoons 1/2\ NO_2^- + 1/2\ H_2O$	14.15
$1/6\ NO_2^- + 4/3\ H^+ + e \rightleftharpoons 1/6\ NH_4^+ + 1/3\ H_2O$	15.14
$1/5\ NO_3^- + 6/5\ H^+ + e \rightleftharpoons 1/10\ N_2(g) + 3/5\ H_2O$	21.05

What do the lines defining O_2 and H_2 represent in seawater? What nitrogen species should predominate in seawater at pE = 12.5 (Sillen) and pH = 8.1 (typical)? How do you account for large amounts of ammonia often found in ocean water. What would horizontal and vertical lines signify on a pE - pH diagram? Give 2 examples of each.

At pH = 8 the reduction of CO_2 to CH_2O occurs at an E_H of about -0.5 V whereas, from your diagram, ammonia is fixed ($N_2 \rightarrow NH_4^+$) at lower electron densities (higher E_H). Why do you suppose plants make such little use of nitrogen fixation for their energy? (Baier)

21. Given that the Beer's law holds for the solution which is measured, it is found that I_o = 33, I = 21, and alpha (a) is independent of d; where alpha is the specific absorption coefficient and d is the pathlength of the cell where the solution is measured, in cm. Calculate the % transmission. You will notice that no units are given above. Why? (Adams)

2. *Water structure*

1. Select 2 of the models for the structure of liquid water and write a brief description of the characteristics of that model. Your description should include the essential aspects of the model, its relationship to experimental data, and the persons who have contributed to the model. Provide a critical assessment of the present status of the model. (Kester)

2. List good and bad points of the Frank & Wen Theory. What is the main evidence in support of this theory today. In the areas that the Frank & Wen Theory breaks down, are there other theories that might offer better explanations? (Loder)

3. Organisms live at the greatest depths of the oceans found today. If the ocean doubled its depth, what properties of water itself at that depth would organisms have to take into account in order to survive? (Loder)

4. There are many experiments that a scientist can perform that give clues concerning the nature of the structure of water. Describe five of these experiments and explain how they have helped our understanding of water structure. (Loder)

5. Relate the structure of water in the vicinity of a cation to that near an anion, a molecule of dissolved gas, a tetramethylammonium ion, and the gas-liquid interface. (Cooke)

6. Name two properties of water which are anomalous compared to other liquids and explain their origin on the basis of the structure of water. (Gordon)

7. What are two of the unusual properties of water? In what ways do these properties affect the environment of the earth's surface? (Kester)

8. One mole of liquid water at 100C is converted into water vapor at 100C. The process occurs under one atmosphere of pressure. The liquid occupied 0.02 liters and the vapor occupies 30.14 liters. A calorimeter showed that Q = 9,717 calories for this process. What was the change in the energy of the system during this process? (Kester)

9. There is no hydrogen bonding in water vapor. The breaking of a hydrogen bond requires 2.6 kcal $mole^{-1}$. From the information in problem 8 calculate the number of hydrogen bonds per molecule in liquid water at 100C. (Kester)

10. Consider 12 moles of water which are distributed in two states. State 1 consists of water molecules with 4 hydrogen bonds; state 2 consists of water molecules with 3 hydrogen bonds. State 1 is arbitrarily assigned zero energy E_1, and state 2 has an energy level E_2. When 10.1 kcal of energy are added to the system with the 12 moles initially in state 1 a certain number of moles, N_2, of water jump to state 2. The entropy at this point is 12.3285 cal deg^{-1} $mole^{-1}$. What is the distribution of moles of water between states 1 and 2 after adding the 10 kcal? How much higher is E_2 above E_1? (Kester)

11. The melting of ice requires 1.44 kcal $mole^{-1}$. If this energy goes into breaking H-bonds in ice, how many H-bonds will there be in liquid water at 0C? (Kester)

12. For the process $(H_2O)_{ice} \rightarrow (H_2O)_{liq}$: ΔH = 1,436 cal $mole^{-1}$; ΔS = 5.257 cal $mole^{-1}$ deg^{-1}. At 1 atmosphere pressure there is a unique temperature, T_f, above which the process goes to the right and below which it goes to the left. Explain, thermodynamically, why this unique temperature must exist and calculate its value. (Kester)

13. For each of the properties listed below, state whether its value for average seawater is less than (<), equal to (=), or greater than (>) its value for distilled water (dw): vapor pressure (of water), chlorinity, surface tension, density, osmotic pressure, thermal expansion coefficient, freezing point, absorption of sound energy, TCO_2 (total inorganic CO_2 concentration), electrical conductivity, temperature of maximum density, and pH (when in gaseous equilibrium with the atmosphere). (Gordon)

14. Why does the temperature of a seawater-ice-salts mixture go down as you "freeze" out the ice and salts while the temperature of a pure water-ice mixture remains constant until all the water has frozen? (Gordon)

15. Calculate the refractive index, freezing point lowering, and osmotic pressure of seawater of chlorinity 19 °/oo. Be sure to identify the source of your formulae and show your calculations. (Gordon)

16. If the vapor pressure of water at some temperature were 20 mm-Hg, what would be the approximate vapor pressure of water over seawater of salinity 35 °/oo at that same temperature? (Gordon)

17. (a) Seawater has been described by one author as a solution of sodium chloride in water, plus a little bit of everything else. Why is water such a good solvent both for electrolytes and non electrolytes?

(b) What property of the water molecule is it that makes such a big difference between the condition a water molecule finds itself in in the gaseous state and in the liquid or solid state?

(c) The latent heat of vaporization of water is higher than its latent heat of fusion. Why?

(d) Why does water have such a low vapor pressure compared to most other compounds of similar formula weight? (Gordon)

3. *Physical processes of the ocean*

1. In the Sargasso Sea warm and light surface water has a thickness of several hundred meters, while at the boundaries, in particular the western boundary, the warm central Atlantic water reduces sharply in thickness leading to marked horizontal density gradients.

(a) How can this observed distribution be explained?

(b) Show schematically how you would expect the isopycnals (lines of equal density) to slope on a vertical section extending from west to east across the Gulf Stream.

(c) Show schematically the changes in the height of sea level on the section mentioned under (b) (Baier)

2. To enrich surface waters with nutrients a cylindrical metal pipe 1 m in diameter by 400 m long is placed vertically with its upper end just below the sea surface. The structure of the water column can be described as follows:

	T, °C	S, °/oo	σ_t	Cp
upper layer	15	35.00	25.99	-0.96
lower layer	8	34.50	26.58	-0.96
also given	8	35.00	27.29	
	15	34.50	25.61	

Initially a pump is used to draw the colder water from the deeper layer towards the surface. Heat is conducted through the tube to the rising water, and when the pump is removed the flow reaches a steady state in which the water emerges at the surface at 14C and the average heat flux through the walls of the pipe is 0.02 calories per cm^{-2} sec^{-1}. Set up appropriate equations, show diagram, and compute the vertical flow rate of the water. State any assumptions used in making your computations and give reasons why this scheme might be impractical or practical. (Baier)

3. (a) The average temperature of the ocean is about 4C. Estimate the rise in sea level that would result if the average temperature of the ocean were raised 10C. What cities might be likely candidates for seaports?

earth radius = 6371 km

ocean volume = 1370 x 10^6 km^3

mean ocean depth = 3.8 km

ocean covers 71% of earth surface

specific volume of 35 per mille 0C seawater = 0.97264 l/kg

specific volume anomaly: 4C = 30 cl/ton

10C = 110 cl/ton

14C = 180 cl/ton

(b) If the ice existing today were melted, how much would sea level be raised? How much would salinity be changed? (Reeburgh)

4. Sketch the main stratification of water masses and their meridional spreading in the cold water sphere of the Atlantic Ocean. Also indicate their origin of formation. (Ku)

5. Indicate by a sketch the zonal and meridional current motions in the warm water sphere. Compare and explain the vertical distributions of T, S, O_2, and σ_t in the warm water sphere of the tropics (e.g., 5^oN) and subtropics (e.g., 30^oN). (Ku)

6. In one region of the world the ocean shows three distinct water masses beneath the surface layer and extending over large areas. The first has a typical temperature of 11.9C and salinity of 36.50 °/oo; the second 2.2 to 3.5C and salinity 34.90 to 34.97 °/oo; and the third shows an almost linear relationship between temperature and salinity with the end points 8.5C, 35.10 °/oo and 19C, 36.70 °/oo. How would these water masses be arranged vertically? Sketch a plot of T and of S versus depth (this latter scale is arbitrary since there are no depths given) on a single depth axis carefully labeling curves and axes. (Hulbert)

7. Plot the station below on a T-S diagram. Indicate mixed layer, seasonal thermocline, main thermocline, instabilities, bed data, and approximate depths and T-S properties of probable core layers, where appropriate. Now given the core layers you have postulated, calculate the percentage of each water mass at the 150 m and 600 m levels.

Depth (M)	Temp (°C)	Salinity (°/oo)	Depth (M)	Temp (°C)	Salinity (°/oo)
0	14.97	34.953	700	7.14	34.493
50	15.11	34.951	800	6.36	34.457
100	11.91	35.079	1000	5.01	34.479
150	11.21	34.995	1250	3.71	34.477
200	10.82	34.942	1500	2.93	34.554
250	10.27	34.872	2000	2.33	34.672
300	10.89	34.867	2500	1.94	34.729
400	8.98	34.675	3000	1.53	34.733
500	8.41	34.599	4000	1.16	34.719
600	7.89	34.549	(Bottom)		

Bonus: Give a guess as to the latitude and time of year of this station. (Hammond)

8. Assuming that water has been released from the solid earth to the atmosphere at a rate proportional to its abundance in the solid earth, i.e. $\frac{d[H_2O]_{earth}}{dt} = -\alpha[H_2O]_{earth}$, calculate ocean volume vs. time for $\alpha = 2.81 \times 10^{-11}\ yr^{-1}$ (found from Ar^{40}). (Hammond)

9. Give evidences from the oxygen isotope data regarding origins of the Antarctic Bottom Water and of the deep waters of the Atlantic, Pacific and Indian Oceans. (Ku)

10. (a) Show how the information in the figure referenced below can be used to crudely estimate the mean turnover time of water in the deep ocean.

(b) In terms of the dynamics of the world ocean circulation, explain why the deep Pacific has a lower C-14 activity than that of the Atlantic.

(Broeker, W. "Chemical Oceanography," 1974, fig 3-3) (Duedall)

11. Despite efforts by the White House to hide them, videotapes are finally released showing that when the astronauts landed on the moon, they found a somewhat small, but relatively deep ocean. On the later Apollo Mission, secret measurements were made of C^{14} and Ra^{226} distributions in this ocean and in the sediment and the air, of air-water CO_2 fluxes both at the very cold polar end (or ends) and at the warmer non-polar end (or middle) and of mixing rates between the surface, deep, and polar regions of the sea. Unfortunately, evil forces have somehow caused the erasure of an 18 minute portion of the tape with all the CO_2 flux and mixing rate data. With the radioactivity data, can you say anything about the physical oceanography of this ocean? Hint: ignore anything that you might think you know about the moon other than the facts given here that it's of identical origin to the earth and that its atmosphere is identical to that of the earth (obviously, any of you who failed to recognize this second fact have been previously mislead by the effete eastern-liberal press and Classics Comic Books). (Sharp)

12. The net photosynthetic production of oxygen is 10×10^{-7} ml O_2 cm^{-2} sec^{-1} in a turbulently mixed region of seawater. This seawater has a steady state concentration of 8.0 ml/l, even though its saturation concentration is 6.0 ml/l, because it is separated from the atmosphere by a laminar layer. The diffusion coefficient of O_2 is 1.2×10^{-5} cm^2 sec^{-1}. The barometric pressure is 754 mm of Hg and the vapor pressure of water is 23 mm of Hg. How thick is the laminar layer? You may neglect any tendency for the supersaturated water to form gas bubbles. (Kester)

13. Thickness of continental ice sheets has a limit of about two kilometers, as has been shown by studies of ice flow in Greenland and Antarctica. Taking this as the average thickness of continental ice sheets during the Pleistocene, and assuming that approximately 10% of the land surface which is now ice-free was ice-covered at that time, calculate the difference in sea level between today and 10,000 years ago. (Hammond)

Here are some useful facts:

Seawater density (35 °/oo, 4C)	1.028 g/cm^3
Total area of the earth	5.1×10^8 km^2
land fraction	30%
sea fraction	70%
Mass of the ocean	1.4×10^{24} gm
Mass of the earth	6.0×10^{27} gm
Rate of river flow to the ocean	1.0×10^{12} gm/sec
Mg^{++} in river water (global ave.)	0.17 mmol/kg
Gravitational acceleration	980 cm/sec^2
1 bar = 0.99 atm. = 10^6 $dyne/cm^2$	

14. Referenced below are profiles of Sr-90 in the North Pacific. The very obvious maxima are near the depth of salinity minimum. Explain the significance of these maxima with respect to what you know about the processes which maintain the integrity of the intermediate water and where the intermediate water is actually formed. (Broeker, W. "Chemical Oceanography," 1974, fig 6-17) (Duedall)

15. Consider a parcel of water that obtains its chemical properties in the surface overflow water between Iceland and Scotland. Trace the path of this parcel as it moves south to the Southern Ocean and finally ends up in the North Pacific. In your discussion please also include a discussion of those physical processes occurring along the path which are dominant in the transfer of any chemical compound from one point to another. (Duedall)

16. Adiabatic mixing in the ocean is usually discussed in terms of T-S diagrams. The following table gives the delta T for equal masses of seawater having initially different salinities.

(a) Based on these data, what can you say about the assumption of adiabatic mixing?

(b) What is the practical significarce of these data?

(c) The data suggests that energy is disappearing; where is it going? (Duedall)

Run #	S(1)	S(2)	delta T (^{o}C)
1	10.0	60.0	-0.067
2	15.0	54.6	-0.041
3	20.0	49.6	-0.021
4	24.8	45.4	-0.010

B. *Composition and General Nature of Seawater*

1. *Salinity*

1. Salinity has been defined by the relationship: S °/oo = 1.80655 Cl. °/oo.
   (a) Briefly describe the evolution of ideas which led to this definition of salinity.
   (b) Is the grams of dissolved salts per kg of seawater greater than, less than, or the same as S °/oo?
   (c) Is the grams of chloride ions contained in a kg of seawater greater than, less than, or the same as the chlorinity of that sample? (Kester)

2. Draw the curve of salt water's freezing point as a function of salinity. On the same plot draw the curve for the temperature of maximum density versus salinity. Does this mean that the whole of the Arctic Basin's water column must be reduced to -1.9C before sea ice can form? Why or why not? (Hammond)

3. Was the recent redefinition of salinity really necessary? Considering the widespread use of STD's, which have precision about equivalent to well-executed chlorinity titrations, the fact that Knudsen's Hydrographical Tables, whether absolutely right for open-ocean work or not, have worked well for over 50 years, the inability to relate the new salinity to absolute density because of the lack of a standard, and the confusion surrounding the redefinition as indicated by the numbers of committee reports and confusing articles, do you think the exercise was worthwhile? (Reeburgh)

4. Discuss the significance of the intercept term in the empirical relationship, S °/oo = 0.03 + 1.805 Cl °/oo. Is the term physically reasonable even though Carritt and Carpenter showed it to be statistically insignificant? (Reeburgh)

5. Calculate the salinities corresponding to chlorinities of 0, 10, 15, 20, 25 °/oo, using the present and old salinity to chlorinity relationships. Carry your work out to five significant figures and tabulate your results. In the same table tabulate the discrepancies between the two sets of salinities. The precision of salinity values determined by first determining chlorinity using the Knudsen silver nitrate titration method was typically about ±0.03 °/oo. The precision of modern salinometry by conductometric methods is typically ±0.001 °/oo or ±0.004 °/oo depending upon the type of instrument employed. Relate these observations to your calculations above. (Gordon)

6. Calculate the contribution by the constituents given in class to the salinity of seawater of salinity 35 °/oo. What is the salinity arising from sodium and chlorine alone? (Gordon)

7. A student measured out 328.5 ml of a seawater sample. He found that 170 ml of a silver nitrate solution containing 100 gm per liter of silver was required to titrate the halides in the sample. Show him how to calculate the chlorosity, chlorinity, and salinity of his seawater sample. (Gordon)

8. An analytical chemist, unaware of the known relationships between chlorinity and salinity wanted to determine salinity of a seawater sample for a friend. He did it the hard way and found the following in a 300 ml sample:

Total solids = 10.8 g/300 ml Br^- = 70 mg/Kg

Organic matter = 10 mg/Kg Density = 1.020 at 20C

HCO_3 = 2.34 x 10^{-3} Molar

He did all his analyses in his 20C lab. What was the salinity? What would the chlorosity (20C) have been if he had known about the Mohr titration? What would have been the chlorinity? (Lower)

9. In the dead of winter a hapless student oceanographer found himself collecting water in the open ocean of the New Hampshire coast. A surface water sample had a chlorinity of 17.5 ppt and a temperature of 3.0C. Later during the summer he returned to the same area and found the chlorinity had changed to 19.3 ppt and a temperature of 17.9C. Using Knudsen's Table, determine the salinity and density for each water sample. Watch the significant figures in reporting answers please. (Loder)

10. From a Mohr-Knudsen titration, you have calculated that the concentration of chloride ion is 18.00 mg/liter. However, you have neglected bromide in the calculations. From the following constants (at. wt. Cl^- = 35, Br^- = 80, I^- = 127, F^- = 19--these have been rounded off for easy calculations) and the constancy of composition for your open ocean seawater sample (Br/Cl = 0.003, F/Cl = 0.00007, and I/Cl = 10^{-7}), answer the following:
    (a) In spite of the low concentration of fluoride in seawater, why can we ignore its contribution to the silver nitrate titration?
    (b) What would be the chloride ion concentration (from your first calculations above) in moles/liter?
    (c) What would be the new chloride ion concentration after you have corrected for the contribution of bromide in your calculations? Express your answer in mg/liter of chloride ion.
    (d) Knowing that the constancy of composition holds for your seawater sample, what is the density of your seawater (the density of pure water at room temperature is assumed to be 1.00 gm/ml. (Adams)

11. Calculate the number of grams of pure silver necessary to precipitate (stoichimetry is 1 mole Ag/1 mole halogen) the Cl, Br and I in 328.5233 g of seawater (S = 35 °/oo) based upon Table 4.1 of Riley and Chester ("Introduction to Marine Chemistry," 1971). Compare this numerical value with the chlorinity by calculating its ratio to the chlorinity. (Hulbert)

12. (a) If you somehow measured the amount of bromide per kg in a sample of seawater, multiplied the amount by the atomic wt. of chloride/atomic wt. of bromide ratio, and added the result to the amount of chloride per kg of the sample, how would this compare to the chlorinity of the sample?
    (b) In what kinds of marine environments would you expect to find deviations from the normal ratio of sulfate to chlorinity? Briefly explain why in each case.
    (c) If you knew how much sodium there was in a sample of seawater how could you tell how much calcium there was in it? What assumptions would you have to make?
    (d) What factors would you have to consider regarding salinity definitions if you were comparing deep salinity data for the same region from an expedition in 1939 with data from an expedition in 1969? How would the data differ numerically if at all? Would the data be comparable? (Gordon)

13. In the open ocean the ratio of sulfate concentration to chlorinity is 0.1400±0.0002, yet in the Black Sea it decreases to values well outside this range. Account for the change in this ratio. Are there gains or losses in $SO_4^=$? In Cl^-? Where do the S and/or Cl atoms originate or where do they wind up? In typical organic matter there is about 1.. moles of sulfur in reduced form for every mole of phosphorus. What is the direction and the relative magnitude of the change in total sulfur-containing inorganic compounds in seawater expected to be (on the basis of the preceeding statement) when organic matter is oxidized? (Hulbert)

14. If a dam were placed at the Strait of Gibraltar isolating the Mediterranean Sea From the Atlantic Ocean, would the Mediterranean be more likely to become a fresh water lake or a saltier lake with the potential to dry up? What evidence do you have for your answer? (Did you know that the only eels that don't reproduce in the Sargasso Sea are those from the Mediterranean Sea and that they do so just east of the Strait of Gibraltar. Think about the significance of that.) (Hammond)

15. Calculate the thickness of a salt layer left by evaporating an ocean of 35 °/oo salinity and 4 km depth. ($\rho_{salt} \approx 2.2$ g/cm^3) (Hammond)

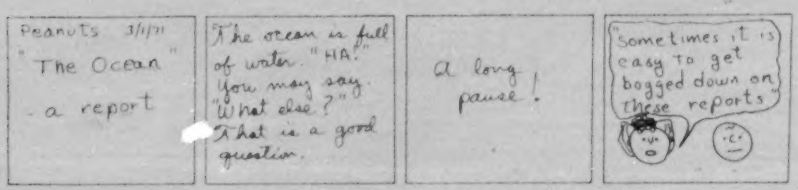
16. Sea level is reported to have been lowered some 300 meters during the last glaciation. If the ocean initially had a salinity of 35 per mille and the water which formed the ice came from the ocean, how would salinity have been affected? Express the change as an absolute value and a percentage of the initial value. (Reeburgh) (Useful information may be found in problem 13, section A.3--ed.)

17. (a) Give an example of an element whose chlorinity ratio is constant. What is its residence time in the oceans? If you do not know it, say so and predict its approximate order of magnitude.
(b) Give two examples of elements whose chlorinity ratios are not constant in the oceans, but each for a different reason. State the reason. Is the residence time concept valid in these cases? Why or why not? (Gordon)

18. Calculate the molality (gm moles per kg of water, not per kg of seawater) of sodium and chlorine in seawater of salinity 35 °/oo. Contrast with the values given in class for the molarities of these ions. Molality is the concentration unit usually preferred in chemical thermodynamics. If you go to that literature for data such as equilibrium constants to use in seawater chemistry calculations, you must be aware of the fact of differing systems of concentration units. (Gordon)

2. Major and minor ions

1.


Peanuts 3/1/71
"The Ocean"
a report
"The ocean is full of water." "HA!" You may say. "What else?" That is a good question.
A long pause!
"Sometimes it is easy to get bogged down on these reports"

(As stated in Peanuts comic strip on March 1, 1971)

"What else?" is a good question. List the concentrations of the major dissolved constituents in seawater and explain why seawater is unique among natural waters. (Reeburgh)

2. (a) What are the colligative properties of solutions? What do they have in common? Which are most important to the heat budget of the oceans? Which are most important to the biology of the oceans? Justify your choices.

   (b) Can a non-conservative variable sometimes be considered to be conservative? Explain and give an example. (Gordon)

3. Major sea salt AB is a 2-2 electrolyte (divalent cation and anion) while major sea salt XY is a 1-1 electrolyte. Each is made up as a solution with ionic strength the same as 35 °/oo seawater and you are now asked to discuss these two solutions. If solution AB is 2.16% in salt AB and the second solution is 5.41% in XY, what are the molecular weights of AB + XY? What are salts AB + XY? Solution AB shows a very large increase (with increasing concentration) in relative viscosity while solution XY shows a slight decrease. Why (include distinction between hydration and electrostriction)? Salt solution XY freezes as would be expected while the freezing point of salt solution AB is not as low as would be expected. Why is this? (Sharp)

4. The concentration of what general class of ion pairs will be increased as a result of an increase in hydrostatic pressure? What general class will be decreased? (Cooke)

5. Consider the dissociation of $MgSO_4^o$ (an ion-pair). Assume the free (SO_4) is 0.02 m and that the pK for the dissociation constant is 2.0.

   (a) Write the dissociation reaction for the ion-pair.

   (b) What is the K value?

   (c) Calculate the ratio $(Mg)/(MgSO_4^o)$.

   (d) Give one reason why it is important to know something about the $MgSO_4^o$ ion-pair. (Duedall)

6. Given the following thermodynamic information:

	Standard Free Energy ΔG^o, K cal
$1/2\ O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$	-56.7
$I_{2(g)} \rightarrow I_{2(aq)}$	- 0.7
$I_{2(s)} \rightarrow I_{2(aq)}$	3.9
$1/2\ I_{2(s)} + e^- \rightarrow I^-_{(aq)}$	-12.4
$1/2\ I_{2(s)} + 3H_2O_{(l)} \rightarrow 6H^+_{(aq)} + IO^-_{3(aq)} + 5e^-$	137.8

   Assume all the iodine in seawater is present in some inorganic form (i.e., I^-, IO_3^-, or $I_{2(aq)}$ and that it is in equilibrium with atmospheric $I_{2(g)}$, which has an atmospheric concentration of 10 ng/m^3. Using actual values for seawater pH (8.3) and atmospheric O_2 concentration (0.2 atm), what should the equilibrium concentration of I^- and IO_3^- be in seawater at 25C? (Duce)

7. The stoichiometric stability constants for the formation of NaF^o, MgF^+ and CaF^+ are 6.2, 18.8 and 4.22 at I = 0.7. Using $[Na^+]_T$ = 0.48509, $[Mg^{2+}]_T$ = 0.05516, $[Ca]_T$ = 0.01068 and $[F^-]_T$ = 0.00005, calculate the speciation of F^- in seawater (i.e., the % of NaF^o, MgF^+, CaF^+ and $[F^-]_F$). (Millero)

8. There has been a lot of research on mercury in the environment in recent years. Mercury is found in seawater in very low concentrations with an average total dissolved concentration of about 5×10^{-2} µg/l = $\times 10^{-8}$ g/l = 2.5×10^{-10} M/l). Calculate the amounts of OH^-, F^-, Cl^-, Br^-, and $SO_4^=$ complexes that Hg forms in seawater of 35 °/oo at room temperature. Discard any of the above complexes that are negligible in seawater. Use the following data. Don't forget activity coefficient. Assume S °/oo = 35, room temperature. (Loder)

Complex	log K	log (conc. of Ligand)	γ(of Ligand)
$HgOH^+$	-3.5	-6	0.7
HgF^+	1.0	-4.2	0.7
$HgCl^+$	6.7	-0.3	0.7
$HgBr^+$	9.0	-3.1	0.7
$HgSO_4$	1.3	-1.5	0.1

9. Garrels and Thompson presented a chemical model for seawater at 25C and one atmosphere total pressure. What is the general picture which emerged from their calculations, as it affects Na, K, Ca, Mg, Cl, SO_4, HCO_3, and CO_3. List the cations and anions in order of increasing amount of complexed interactions with other ions. (First ion would be the one that is complexed the least). Give a brief statement of why this is the case. (Adams)

10. A synthetic seawater solution (prepared from pure reagent chemicals) contains the following chemical species:

Species	Molality	Species	Molality
Cl^-	0.566	$MgSO_4^o$	0.006
Mg^{2+}	0.050	$CaSO_4^o$	0.001
SO_4^{2-}	0.011	Br^-	0.001
$NaSO_4^-$	0.011	Na^+	
Ca^{2+}	0.010		

(a) What is the molality of sodium ion species, Na^+?

(b) What is the ionic strength of this solution? (Kester)

11. A NaCl solution was made up with distilled water such that its ionic strength matched that of seawater (~0.71).

(a) What is the molality of the resulting NaCl solution?

(b) Would you expect its freezing point to be lower or higher than that of a $MgCl_2$ solution of equal ionic strength? Why? (Baier)

12. The following are all at 25C.

(a) Calculate and plot values of the activity coefficient of the assigned electrolyte over the range $0 \leq I \leq 2$ based on the Debye-Hückel equation, the Stokes-Robinson hydration equation, and experimental values.

(b) Plot the values of the activity coefficient of the assigned cation based on the MacInnes assumption and the Bates, Staples, and Robinson method for the range $0 \leq I \leq 2$. (Kester)

Assigned Electrolytes

Electrolyte	h	a	Electrolyte	h	a
HCl	8.0	4.47	$MgCl_2$	13.7	5.02
LiCl	7.1	4.32	$CaCl_2$	12.0	4.73
KCl	1.9	3.63	$SrCl_2$	10.7	4.61
NH_4Cl	1.6	3.75	$BaCl_2$	7.7	4.45
RbCl	1.2	3.49	$CdCl_2$	12.0	4.73

13. Calculate the molarity of Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, $SO_4^=$ in seawater of 19 °/oo chlorinity and sum the positive and negative charges. Do they balance? (Hammond)

14. Calculate the molal concentration of the eleven major ions in seawater of 35.000 °/oo salinity. (Kester)

    Relationships to be used in the calculation:

    1. S °/oo = 1.80655 Cl °/oo
    2. Moles of A = (g of A)/(ionic weight): (ionic weight is the same as the atomic weight for a monatomic ion; it is the sum of the atomic weights for a polyatomic species.)
    3. Cl °/oo = 0.3285234 · (g of Ag)/(kg of seawater)
    4. Moles of Ag = moles of Cl^- + moles of Br^-
    5. (g of H_2O)/(kg sw) = 1000.000 - (g of ions)/(kg sw)
    6. Molality of A = (moles of A)/(1000g of H_2O)

15. The table below indicates changes in molar enthalphy, entropy, and volume which occur when a mole of various ions are placed in a large quantity of water. Provide a conceptual interpretation of the significance of these ΔH, ΔS, and ΔV values and suggest a molecular model which is consistent with them. Your considerations should include the general magnitudes of the thermodynamic changes as well as the variations observed among the different ions.

Ion	Pauling Radii Å	ΔH^a Kcal $mole^{-1}$	ΔS^a cal deg^{-1} $mole^{-1}$	ΔV^b cm^3 $mole^{-1}$
Na^+	0.95	- 95	-20.9	- 5.7
K^+	1.33	- 75	-12.4	+ 4.5
Mg^{2+}	0.65	-456	-64	-30.1
Ca^{2+}	0.99	-377	-50	-26.9
Cl^-	1.81	- 90	-23.5	+22.3
Br^-	1.95	- 82	-19.5	+29.2
I^-	2.16	- 71	-14.3	+40.8

[a]Hunt, J.P. 1963. Metal Ions in Agneous Solutions, Benjamin. p. 16, 124 pp.

[b]Millero, F.J. 1969. Limnol. Oceanogr. 14(3): 376-385 (Kester)

16. Consider a volume of 1,009 cm^3 of seawater which will contain 1,000 grams of H_2O and which will consist essentially of the following ions:

Ion	Molality	Ion	Molality	Ion	Molality
Na^+	0.48	K^+	0.010	SO_4^{2-}	0.029
Cl^-	0.56	Mg^{2+}	0.055	Ca^{2+}	0.010

What percentage of the water molecules will be in the hydration spheres of the ions? Indicate the basis for your calculations and any assumptions or guesses you may have to make. (Kester)

17. (a) Typical seawater is approximately a 1/2 molar solution of salts, chiefly sodium chloride. It freezes at about -1.86C. A 1/2 molar sugar solution freezes at -0.9C, approximately. Explain.

(b) List the first five most abundant elements in seawater in order of decreasing concentration in terms of weight of element per kg of seawater. Think about this before you write!

(c) Are the salts dissolved in seawater completely dissociated? Explain, using only quantitatively significant examples or facts.

(d) List four elements or ions whose concentrations relative to chloride (chlorinity ratios) you would expect to be constant in the oceans.

(e) List four whose chlorinity ratio you would expect to vary.

(f) Why can so much sea salt be dissolved in water (up to 30-40 gm/kg) and so little petroleum-like matter (a few mg/kg at most)? (Gordon)

18. List the major constituents of seawater under the heading in the table below which best describes our present knowledge of the variability of that constituent's chlorinity ratio. (Kester)

Cl °/oo ratio is constant within present analytical techniques	Cl °/oo ratio varies relative to present analytical precision	Constancy of the Cl °/oo ratio cannot be assessed at the present time

19. Using information supplied in Millero, The Sea v. 5, calculate the volume and weight ionic strength for seawater. Derive a combination of the salts (NaCl, KCl, KBr, NaF, Na_2SO_4, $MgCl_2$, $CaCl_2$, $SrCl_2$, $NaHCO_3$ and H_3BO_3) that can be used to make synthetic seawater (35 °/oo S). Why doesn't gm/Kgm SW not equal 35.000? Why don't these molality and molarity concentrations yield reasonable values for Baltic Seawaters (i.e., Kundsen's work)? Demonstrate the law of electroneutrality using these results. (Millero)

20. A sample of seawater is saturated with $BaSO_4$ (barium sulfate). Calculate the concentration of total barium, T(Ba), dissolved in this seawater. The following information may be useful: (Kester)

Solubility product of $BaSO_4$ = K_{sp} = $a_{Ba}\, a_{SO_4}$ = 4.32×10^{-10}

Total sulfate at saturation = $T(SO_4)$ = 0.030 molal

Free Sulfate = $[SO_4^{2-}]$ = 40% $T(SO_4)$ Free Barium = $[Ba^{2+}]$ = 90% T(Ba) (a_x is the activity of x)

21. (a) Why do we not obtain iodine directly from seawater, instead of from marine plants or nitrate deposits, just as we do bromine?

(b) Write the chemical equation used in industry for recovery of iodine or bromine from seawater. (Gordon)

22. You have been exposed to the old Norse folktale that the sea is salt because somewhere on the bottom of the ocean a magic salt mill is steadily grinding away. Probably no one (at least, no reputable chemical oceanographer) is really sitting down on the bottom of the ocean grinding away at that mill. Yet, the ocean is salty and the old Norse tale has a profound ring to it. From whence cometh the salt (and water) and why are there relatively constant proportions of the major sea salts? (Sharp)

23. (a) Where has the salt of the seas come from?
(b) What lines of evidence support your conclusions?
(c) How has the sea come to have its present average pH?
(d) Where did the molecular oxygen of the earth come from?
(e) Have the oceans always had their present salinity, pH, and dissolved oxygen concentration? Explain. (Gordon)

24. What is the most likely source to the ocean over geologic time of each of the major constituents of seawater? (Sodium, chloride, magnesium, calcium, potassium, sulfate, bicarbonate, bromide, strontium, boron, fluoride). (Kester)

25. Goldschmidt used the method of geochemical balance to arrive at the composition of 1 liter of seawater. What class of components did Goldschmidt have to add to his balance sheet in order to achieve a true balance? Identify four of the five compounds in this particular class. (Duedall)

26. Most salts are added to the ocean in the surface waters by river input and are thought to be removed by processes at the bottom of the ocean. However, the only concentration gradients observed appear to be due to addition or removal of H_2O (i.e. salts have constant ratios to Cl^- everywhere in the ocean). Explain this dilemma. (Hammond)

27. It is curious that the relative composition of gases from volcanoes shows that CO_2 is in significantly higher concentration than Cl_2 yet we find that Cl in seawater is in much higher concentration than the sum of CO_2, H_2CO_3, HCO_3, and CO_3. Explain this. That is, where is all the carbon? (Duedall)

28. Show by simple calculation that hot springs discharge from continents and ocean floor is sufficient to account for the present mass of the water in seawater. Discharge rate = 6.6×10^{16} g/hr. (The present mass of water is approximately 10^{24} g.) (Duedall)

29. List the major constituents of the ocean in order of decreasing abundance (by weight). (You should have 8). You may group these elements in a convenient manner and suggest the paths these groups have followed between earth accretion and accumulation in the ocean. (Hammond)

30. Draw a diagram illustrating the geochemical cycle of Na^+ on the earth, labeling the reservoirs and the transportation routes. (Include the earth's crust). (Hammond)

31. Approximately 1 kg of sedimentary rocks exist for each kg of water in the ocean. The concentration of Boron in igneous rocks is approximately 10 ppm by weight, and greater than this in sedimentary rocks. The boiling point of $B(OH)_4$ is 300C at 1 atmosphere pressure. What is the probable source of Boron in seawater? (Hammond)

32. What is a steady-state situation in the ocean as opposed to an equilibrium situation. Assuming that steady-state can be achieved, why does sodium reach steady-state in 600 million years while potassium reaches steady-state in 30 million years? Why would the sodium to potassium ratio have been rising during the last 600 million years? (Cooke)

33. If the potassium content of igneous rock was ten times its present value, what would you expect the composition of the ocean to be today? (Cooke)

34. Describe the present view of the history of the cation content of the sea relative to that of the anions. (Cooke)

35. Compare the evolution of seawater during the history of the earth before the industrial revolution with its evolution since the beginning of the industrial revolution. (You may wish to consider such aspects as the rate of accretion of the ocean, its salinity, pH, trace metal composition, nutrient concentrations, etc.) (Gordon)

36. The composition of seawater is quite different than that of river water. Furthermore, the composition of seawater seems to have been nearly constant over the last several million years. Thus it has been proposed that some mechanism(s) operates to fix the abundance of each component of seawater. Name 2 types of mechanisms and give a specific example of each. (Hammond)

37. What point do you have to keep in mind when you use data on the accumulation of volatiles for the verification of the Rubey theory for the origin of the ocean? (Duedall)

38. Give some convincing thoughts as to why the "slow-soak" hypothesis for the accumulation of excess volatiles is preferred over the "quick-soak" hypothesis. (Duedall)

39. I once received a letter from a high school student. He said that he had put two wires, connected to a battery, into a glass of seawater. He said that gas bubbles were formed at both wires and one quickly became covered with a white stuff. Explain his observations. Hint: $Mg(OH)_2$ precipitates from seawater if the pH goes above 9.5 or so. (Assume that he was rich and used wires made of platinum or gold so that the wires didn't react chemically in any way.) (Gordon)

40. (a) Give the probable course of events when a shallow lagoon fills with seawater and dries up completely.
(b) What would happen if only half the water evaporated before the lagoon was refilled and rather thoroughly flushed and the whole cycle repeated itself for a long time?
(c) If 95% of the water evaporated before refilling and flushing and this cycle repeated itself? (Gordon)

41. You have just recovered an N.I.O. bottle from the hydrowire. Outline what steps you would take to obtain water samples for chemical analyses (which samples you would collect first, how you would handle each sample, and how they would be treated for later analyses in the shore-base laboratory). Organize your approach to answering this question, and present the material in a concise, easy-to-follow, outline. (Adams)

3. Trace elements

1. Discuss in outline form the various methods of transport, pathways and mechanisms by which a trace metal dumped by the Amalgamated Bilgewater Co. into a river on a small estuary makes its way into the sediments of the continental shelf. Discuss the odds of making it to the deep sea... (Loder)

2. Construct a model for the chemical speciation of the assigned trace element in seawater. Indicate whatever assumptions or judgments are necessary for your calculation. Your calculation should consider the oxidation state, the major inorganic species, and an assessment of the significance of possible organic complexes of the selected element. (Kester)

3. An abundant pelagic organism in the polluted upper Beerfoam Bay has an alarmingly high Zn concentration and it makes a $SrSO_4$ shell. Once the organism is flushed from the bay to the neighboring ocean, its zinc content drops markedly. Why? Normally $SrSO_4$ is soluble in most natural waters. How does the organism survive being dissolved? It has been observed that there are no $SrSO_4$ tests from these organisms in the bay sediments but there are in oceanic surface sediments. Why is this? (Sharp)

4. Explain the observation that manganese nodules are not found on the sea floor where the water adjacent to the deposits has a detectable sulphide content and/or where the sedimentation accumulation rates are high. (Ku)

5. Magnesium is being added to the ocean by weathering of crustal rocks. Its concentration (corrected for cyclic salts) in rivers is about 0.3 meq/l. It has been suggested that clay minerals serve as a sink for oceanic Mg^{++}. The cation exchange capacity (i.e. the total number of cations which are readily exchanged) of clays found in rivers is about 50 meq/100 gms. Evaluate river clay as a sink for Mg^{++} and discuss the significance of your calculation. The following will be helpful: (Hammond)

Average sedimentation rate of deep sea clay	1×10^{-3} gm/cm^2 yr^{-1}
Area of ocean	3.5×10^{18} cm^2
Rate of river flow	3×10^{16} kg/yr

6. What is the predominant species of mercury in a plating waste consisting of approximately 0.01 M NaCN and 0.002 M $Hg(NO_3)_2$? Describe the probable environmental fate of this waste when it is poured down a sewer, subjected to anerobic digestion in the sewer pipes, treated with chlorine to kill pathogenic bacteria, and dumped into Boston Harbor. What is the predominant mercury species in the water of the harbor? (Butler)

4. Residence times

1. (a) Upon what assumptions does the calculation of oceanic residence times depend?
   (b) Are any of these assumptions made invalid in the case of a residence time that we calculate as 10^4, or 10^1, years? State the basis for your conclusion, in each case.
   (c) Discuss the relationship of the residence time of an element to its chemical reactivity in the oceans. (Gordon)

2. (a) What do you have to know in order to calculate the residence time of an element in the oceans?

   (b) Which classes of elements have the longest residence times in the oceans? Why do you think this is so?

   (c) What are "cyclic salts"?

   (d) If one ignores the existence of cyclic salts, what happens to the residence times he calculates for sodium and for aluminum?

   (e) Give one example each of an element of long, short, and intermediate residence time. Give the order of magnitude of the residence time of each. (Gordon)

3. (a) What is meant by steady state? Explain mathematically.

   (b) Give a reasonable explanation why Ca has a shorter residence time than Na.

   (c) Assume element X has a concentration of 0.5 molal and that the volume of the world ocean is 10^{24} cm^3 and the rate of addition of X is 5×10^{12} moles/yr. Calculate the residence time (τ_x). What can you say about the reactivity of X in the marine environment compared to Na. (Duedall)

4. A new element oceanorium (Oc) was discovered by Professor Zooke after dissolving 10.0 kg of Ralfus oroarki (a pelagic foraminifera found only in the open ocean) in HCl and running the HCl through a chelating resin. He was able to recover 2.5 mg of the element. Then after collecting 1000 liters of seawater and extracting he found only 500 micrograms of oceanorium. Assuming a density of 1.025 for the seawater, what was the biological concentration factor?

   He later found (Zooke and Smedley, 1972) that oceanorium was only found in Ralfus O. and that this foram was found only in an area (10^6 km^2) west of Africa with an average depth of 3000 m. They discovered that the average annual production of Ralfus O. was 50 mg/m^2 surface area. It made up only 0.5% of the sediment by weight. The sedimentation rate was determined to be 1 cm/1000 years, which was equivalent to 2×10^3 grams of sediment/m^2/1000 yr. What percent of the total oceanorium was tied up in Ralfus O. and what is the residence time of oceanorium? (Loder)

5. Discuss the consequences of the residence time of water in air being about ten days, while the residence time of carbon dioxide in the sea is about ten years. (Cooke)

6. Calculate the sedimentation residence time, τ_{sed}, for the following various particle sizes: 2.6, 4.0, 6.5, 10, 16, 26, 40, 65μ; assuming a 2.5 km height distribution for the particles. In addition, calculate the overall residence time of the particles taking into consideration rainout, assuming a mean rainout residence time of 4 days. (Duce)

7. The rate of oxidation of H_2S by ozone is dependent upon both the ozone concentration and the total particle surface area per unit volume of air. The exact relationship is as follows:

$$-d[H_2S]/dt = k[O_3]^{1.5}[A]^{0.5}$$

   where $k = 2 \times 10^2$ $cm^2/mole^{0.5}$ sec. [A] = Surface area of particles, in cm^2, per cm^3 of air

   $[O_3]$ = Ozone concentration (0.05 ppm) $[H_2S]$ = H_2S concentration (1.0 ppb)

   Calculate the residence time of H_2S in the atmosphere over the ocean and over the continents, assuming that the only removal mechanism is oxidation by O_3, and using the particle size and number distributions given below. (Duce)

Radius (cm)	Continents (#/cm^3)	Ocean (#/cm^3)	Radius (cm)	Continents (#/cm^3)	Ocean (#/cm^3)
7×10^{-7}	1600	3	7×10^{-5}	29	2
2×10^{-6}	6800	83	2×10^{-4}	0.94	0.47
7×10^{-6}	5800	105	7×10^{-4}	0.0029	0.0029
2×10^{-5}	940	14			

Note: All concentrations are in moles/cc of air. For your surface area calculations, assume that the particles are all present in discrete groups with the radii and number indicated.

8. Given the following information:

Br/Na ratio on sea salt particles collected in marine air = 4.0×10^{-3};

Br/Na ratio in seawater = 7.0×10^{-3};

Gaseous Br concentration in marine air = 50ng/m^3;

Particulate Br concentration in marine air = 10ng/m^3;

Particulate Br residence time in marine air (after initial rapid gas loss) = 5 days.

Assuming atmospheric sea salt particles produced by the ocean initially have the seawater Br/Na ratio but very rapidly (seconds to minutes) lose Br to the gas phase, reaching some type of equilibrium at a Br/Na ratio of 4.0×10^{-3}, and assuming all the gaseous Br comes from this source, what is the atmospheric residence time of gaseous Br? (Duce)

9. In 1963, nuclear testing released large amounts of C^{14} to the atmosphere, enough to increase the atmospheric C^{14}/C^{12} ratio by 6%. This "spike" of C^{14} originated in Nevada. Using your knowledge of the residence time of carbon in various geochemical reservoirs, do you expect the "spike" to be well mixed within: (1) the atmosphere, (2) the biosphere, (3) the deep ocean? (Hammond)

10. (a) To compute the residence time of water in the deep ocean on the basis of C^{14}/C^{12} ratios requires what assumption about the C^{14}/C^{12} ratio in the atmosphere?

(b) How do we know this is so? (Hammond)

11. Show that the definition of residence time given by

$$\tau = \frac{\text{amount present}}{\text{rate removed}}$$

describes the time to remove 1 - 1/e of a pollutant added to a perfectly mixed ocean.

Bismuth has a residence time of 4.5×10^4 yrs (Goldberg, 1965) and a concentration of 0.02 ppb in the ocean. How well would Bi added to the ocean be mixed? If this addition were equal to the present inventory of Bi in the ocean and were made up totally of 208 Bi, a nuclide with a half-life of about 8×10^5 yr, when would half of the total bismuth in the ocean be removed assuming no more of the element enters or is produced in the ocean after the time of this addition? Using your derived equation, plot the values of Bi versus time. (Baier)

12. On the basis of residence times, for which of the following elements would you expect to see variations in their ratios to Cl^- in different parts of the ocean? Na, Mg, Fe, Mn, Ra^{228} (7 year half life), Ra^{226} (1600 year half life), U^{235} (0.7 year half life) (Hammond)

13. If deep ocean water is manufactured at a rate of 30 sverdrups (1 sverdrup = 10^6 m^3/sec), what is the residence time of water in the deep ocean (z = 200 M to 4000 M)? (Hammond)

14. From the previous problem, what must the residence time of water be in the surface ocean (0 to 200 M)? (Hammond)

15. Sediments contain approximately 0.6% carbon in organic material. For an average sedimentation rate of 2 cm/10^3 yrs, calculate the ratio of carbon removed in shells to carbon removed in organic compounds. Calculate the residence time of carbon in the whole ocean. If P is removed in organic compounds which have the same C:P ratio as tissue, calculate the residence time of P in the whole ocean. (Hammond)

16. The following table lists the residence time and the variability in the chlorinity ratio for several elements in the ocean.

Element	Variability of Chlorinity Ratio*	Residence Time (Year)	Element	Variability of Chlorinity Ratio*	Residence Time (Year)
Sodium	0.3%	2×10^8	Nickel	50%	2×10^4
Magnesium	0.3%	3×10^7	Silicon	100%	8×10^3
Calcium	1 %	4×10^6	Manganese	800%	1×10^3
Rubidium	10 %	3×10^5	Iron	800%	1×10^2

*Variability in percent is $\frac{\text{Maximum value - Average value}}{\text{Average value}} \times 100$.

(a) How do you think the relationship between the variability of the chlorinity ratio and residence time can best be described?

(b) What does this relationship reveal about oceanic processes? (Kester)

17. Calculate the residence time of fluoride in the ocean. You may find the following information useful:

(a) The worldwide average concentration of F^- in river water is 0.15 mg F/l.

(b) Rivers discharge 3.2×10^{16} l of water to the oceans each year.

(c) The volume of the ocean is 1.37×10^{21} l.

(d) Assume that aerosol formation from seawater leads to a 100 fold enrichment of F^- over Cl^- in the sea salt particle.

(e) Volcanic input of fluoride may be estimated as 1.0×10^{12} g per year. (Kester)

18. Calculate the length of time it takes for carbon to get from the surface water to the upper sediment layer if the ratio of ^{14}C in these two locations ranges from 100:1 to 1000:1.

$[N/N_o = e^{-0.693t/t_{1/2}}, \quad \ln e = 1.00, \ln X = 2.303 \cdot \log X]$

What chemical reactions allow ^{14}C to go from the water to the sediments? (Hulbert)

19. Suppose that the per capita rate of introduction of cadmium into the ocean were, for all of the 666 million people whose wastes flow to the North Atlantic, the same as that for urban Californians: 2.6×10^{-6} pounds/capita-day. (For the purposes of this problem, you may take the area of the North Atlantic to be 2/5 that of the whole Atlantic.) How would the yearly input of cadmium into the surface layer (upper 200 meters) compare with the amount currently present? The water of the surface layer has a residence time of approximately 20 years. What would the expected residence time of cadmium in this surface layer be, and why? (Hint: Consider why the residence time might be altered from what it currently is.) (Hulbert)

20. Suppose that the annual river water input to the oceans is 3×10^{16} kg. Using the necessary data from Riley and Chester (1971), (table 4.1), calculate the oceanic residence times of water and aluminum. Assume that the average salinity of the oceans is 35 $^{o}/_{oo}$. From your notes, the mass of the oceans 1.4×10^{21} l. (Gordon)

21. Using Livingstone's figure for the annual net transport of sodium to the sea of 10.7×10^{7} tons per year and Clarke's estimate for the amount of sodium in the sea, 14.1×10^{15} tons, calculate the residence time of sodium in the sea.

    (a) What assumptions are involved in this calculation? Are the assumptions valid? Why?

    (b) Had you obtained a figure for the residence time of aluminum and it came out to be 100 years, what then? Would the assumptions still be valid? Why or why not? If not, then what would be the significance of the residence time you calculated for aluminum? (Gordon)

22. Using the data in Table 1 of Goldberg's article (The Sea, v. 1), interpret the residence time values for each element. Give a 2-4 sentence explanation, if possible, for each element for which data exists. (Duedall)

C. Gases

1. Atmosphere and exchange processes

1. Given the following points on an atmospheric sounding:

P (mb)	T (°C)	e (mb)	P (mb)	T (°C)	e (mb)
1020	22	18	200	-50	--
800	15	6	120	-65	--
600	1	2	80	-60	--
360	-28	0	40	-60	--

(a) Find the atmospheric pressure P at the 20 km level.

(b) Find the total pressure, P, and the percentage composition of the atmosphere at the 100 km level. For this make the following assumptions:

(1) q_m and G are essentially equal

(2) there is no vertical mixing of air above 20 km, only molecular diffusion

(3) the temperature remains at -60C to the top of the atmosphere

(4) the percentage composition of the atmosphere at 20 km is the following (by volume):

N_2 = 78%; O_2 = 21%; Ar = 0.94%; CO_2 = 0.04%; H_2 = 0.02%. (Duce)

2. Given an atmosphere in which $\frac{dt}{dz}$ = -6.5° C/km (the world average) and whose surface temperature is 30C (not the world average), if a parcel of air is saturated at 28 grams of H_2O per kilogram of air and through some perturbation rises 500 m, losing one gm of H_2O per kg of air through condensation, what motion is that air parcel likely to experience? Why? Show your work.

Now using your knowledge of continuity, how is this likely to affect the motion of nearby air? As time goes on is it likely to be rainy? Is it likely to be windy? What might this natural phenomenon be called? What is its energy source? Is it a perpetual motion machine? What is intrinsic to it that limits its life span? (Hammond)

3. Compute the atmosphere's density knowing that a column of water about 10 meters deep exerts the same pressure as a column of the atmosphere from top to bottom. Assume that the atmosphere is homogeneous and its top is 10 km high. (This is a bad assumption but if it were homogeneous, and everywhere as dense as at sea level, the atmosphere would be about 10 km high--makes everything simple to remember). (Hammond)

4. Show on a T vs. Z plot the (a) dry adiabat, (b) a typical moist adiabat, (c) an example of a stable environmental temperature curve, (d) an unstable atmospheric curve, (e) $\frac{d\theta}{dz}$ where θ is potential temperature, and potential temperature curves for both the (f) stable and (g) unstable cases. (Assume atmosphere is dry for all environmental curves, label your axes, and consider only the lower troposphere). (Hammond)

5. Given a saturated parcel of air at sea level (1 atmosphere or 1000 mb) and 10C, if we raise this parcel of moist air adiabatically to 1 km above sea level the temperature drops to about 4.5C and the moisture content goes from about 8 gm/kg of air to about 6 gm/kg of air. The dry adiabat is -10° C/km. What is the wet adiabat? Is it what you'd expect knowing that the latent heat of vaporization L = 600 cal/gm and the specific heat of air ≈ 1/4 cal/g/°C. Show your work. (Hammond)

6. If cloud cover increased from 50% to 75% (and assuming clouds' albedo averages 50%) what would the new percent of the solar constant that reaches the earth surface be (assume only albedo is affected). Now if the earth's surface temperature somehow remained the same, what must happen to p, the long wave back radiation window percentage of the total flux back from the surface. Calculate the new p. Is it possible p might change this way with an increased cloud cover? How? (Hammond)

7. Assuming a real earth ($T_{surface} = 288^{0}$ K, calculate p (the effective percentage that the earth's long wave back radiation window comprises of the total energy flux from the earth's surface. (Hammond)

8. Calculate the Solar Constant, i.e. the solar flux at the top of the earth's atmosphere. Use any of the following information: (Hammond)

$T_{sun\ surface} = 6000^{0}$K $\quad \sigma = 1.4 \times 10^{-12} \frac{cal}{cm^2 \cdot sec \cdot deg^4}$ $\quad r_{earth} = 6 \times 10^{3}$ km

$r_{sun} = 7 \times 10^{5}$ km $\quad R_{sun\ to\ earth} = 1.5 \times 10^{8}$ km

9. The land and water surfaces of the earth receive more heat through radiation than they give up by radiation. Explain why there isn't a general heating with time. (Hammond)

10. When a hurricane crosses a coastline and passes over land its destructive force rapidly decreases and the deep low pressure area disappears altogether in a relatively short time. What factors might account for the rapid break-up of hurricanes over land? (Duce)

11. There are a number of factors which determine the pollution level in an urban area at any time. One of these factors is the general meteorological situation, for example, whether the area is under the influence of a high pressure system or a low pressure system. Under which of these two systems are the highest levels of air pollution usually found in an urban area, and why are the levels higher under one system than the other? (Duce)

12. Low pressure areas with strong pressure gradients and accompanying strong winds are quite common in the atmosphere. High velocity winds are not observed around high pressure areas, however. Explain why this is so, as simply as possible, using either physical reasoning or mathematical equations. (Duce)

13. Man is injecting a wide variety of substances into the atmosphere. If you had the opportunity to stop the injection of just one of these substances on a worldwide basis, which one would you pick and why? (Duce)

14. If somehow the total pressure of the atmosphere suddenly doubled, what would be the effects on the chemistry of the oceans? Assume that the composition of the atmosphere remains unchanged. (Gordon)

15. The earth and Mars have similar "decompressed" densities, indicating that their bulk compositions may be quite similar. The mass of Mars is only 0.1 times the mass of the earth and its radius is 0.5 Re. Why doesn't Mars have an atmosphere? (Hammond)

16. The stagnant boundary model predicts that the time constant for gas exchange is $\tau = \frac{zh}{D}$, where z = stagnant film thickness, h = mean depth of the well-mixed surface layer, D = molecular diffusion constant of the gas in question. For nearly all gases, D = 1-2 x 10^{-5} cm^2/sec and z is close to 30μ. Calculate the time constant for O_2 in the surface ocean (approximately).

Gas solubility is a function of temperature. If O_2 was not consumed in the deep ocean, what concentration would you expect (in terms of σ_T)? (Hammond)

17. Show how jet drop ejection into the atmosphere occurs (from Horne, p. 348) and show a mechanism for the ejection of positive electrification with the jet droplets (shown in Horne, which is taken from Blanchard). (Adams)

18. We have seen how much disagreement there is between the only two serious estimates of the annual production of atmospheric sea salt particles. Assuming you had to make a new estimate and had relatively unlimited research funds and facilities at your disposal, how would you go about making your estimate? What would you do that would make your estimate more accurate than Blanchard or Eriksson? (Duce)

19. Given Woodcock's (1953) figure on atmospheric sea salt concentrations at various wind speeds and Eriksson's tables on fall velocity, etc., calculate both the number and mass of sea salt particles of various sizes falling onto 1 cm^2 of the sea surface per second due to sedimentation. Make these calculations for 0.2 log D intervals for particle diameters (at 91.4% relative humidity) of 2.6, 4.0, 6.5, 10, 16, 26, 40, and 65μ. In addition, obtain the total number and mass fallout for all the sizes above. Make your calculations for only one of the following wind speeds: Force 3 (mean speed 9 Kts), Force 4 (13 Kts), Force 5 (18 Kts), or Force 7 (30 Kts). (Duce)

20. Explain in your own words why you may, or may not, think that gas injection is a non-thermodynamic process. (Duedall)

21. Assume air injection is occurring in the South Atlantic; show how you would set up equations to calculate the effect of injected air on the density of seawater. (Duedall)

22. Assume seawater has a surface tension of 74 dynes/cm, and also assume that water in a particularly rough area of the North Atlantic Ocean is supersaturated with air by 3%, i.e. it is 103% saturated at a particular temperature, T. What is the diameter of the largest bubble which will not tend to dissolve in this water at temperature-T? (Duce)

23. Amalgamated Bilgewater Corp. of Hackensack, NJ, has not so unwittingly allowed 2 x 10^7 tons of a noisome monomer to be flushed to the sea. This stuff lies on the surface and is slowly polymerized by sunlight to form a tough crinkly film. The film is fortunately edible by whelks and periwinkles. How is the weather in London affected by AB Corp.'s corporate wisdom? (Cooke)

2. *Non-carbon dioxide gases*

a. Analytical methods

1. (a) How may one estimate the amount of oxygen which has been consumed from a sample of seawater collected from depth in the ocean?

(b) Are there limitations to the method you have described above? If so, suggest an approach to overcome these limitations. (Meyers)

2. What is the Winkler method? Give the pertinent equations (balanced), discuss possible errors, their directions and steps that can be taken to remedy them. Give two types of oxygen standard in current use. (Reeburgh)

3. In the formula used for calculating the concentration of oxygen during the Winkler titration, the amount of reagents added (manganous sulfate and alkaline potassium iodide) are accounted for by subtracting them from the volume of the sample. Why didn't we allow for the one ml of sulfuric acid which is also added to the solution? (Adams)

4. You have sampled and analyzed a water sample for oxygen. The measured value is 7 ml/L. In a duplicate sample you accidentally trap a 4 mm diameter air bubble after the manganese and iodide are added. If the bottle contains 150 ml and the bubble reacts quantitatively with the reagents, how big an error will result? How does this error compare with failure to account for oxygen added with reagents? (Reeburgh)

5. A sample is titrated according to the Winkler method to a clear endpoint, and it is found that 3.60 ml of sodium thiosulfate is required. You then return to your lab bench after a few minutes and notice that the solution is now slightly blue. What should you do? (Given the normality of the thiosulfate = 0.085, burette is 10 ml with correction factor of 0.011 ml at 3.6 ml mark, temperature in the lab is 24.5C, and the density of the solution is 1.00). (Adams)

6. In the equation for determining the concentration of oxygen after the Winkler titration, i.e.,

$$\text{ml. } Na_2S_2O_3 \times N \times \frac{8}{16} \times \frac{1000}{S \times \frac{B-2}{B}} = \text{mg. at. of } O_2$$

the 2 was used as a reagent correction. What reagents was this referring to, and why is it included in the equation? (Adams)

b. Distribution and concentration

1. What would be the effect on the concentration of oxygen (O_2) and nitrogen in a beaker of seawater which is in contact with the atmosphere if you did the following things and waited for equilibrium to be re-established after each change in conditions (Briefly justify each conclusion): (a) increased the atmospheric pressure? (b) evaporated away some of the water? (c) cooled the water to near the freezing point but didn't freeze any? (d) continuously bubbled pure nitrogen or pure oxygen through the solution? (e) stirred the water violently so that many air bubbles were drawn into the seawater? (f) replaced the air with pure oxygen or pure nitrogen? (g) replaced the nitrogen in the air with an equal concentration of pure argon? (Gordon)

2. Harvey (1955) shows on p. 32 that a large part of the deep water in the eastern basins of the Atlantic Ocean contains dissolved oxygen at levels of 5.25 cc per liter. To what concentration in (μmol/kg) does this correspond? (Gordon)

3. What will be the concentration of oxygen in millimoles per kg of seawater (salinity 35.00 ‰) in a sample of seawater equilibrated with moist (100% relative humidity) air at a total pressure of one atmosphere, when the temperature of equilibration is 20C and at 0.5C? Use as the density of the seawater, 1.025 and 1.028, respectively. (Gordon)

4. (a) How would you determine whether or not seawater at a given depth and place in the ocean is saturated with oxygen? How might you express the result?

(b) Two samples of seawater were found to contain: A: 12.6 ml of N_2 and 2.0 ml of O_2 per liter, and B: 11.5 ml of N_2 and 6.5 ml of O_2 per liter.

(c) What can you say about the previous histories of the waters of the oceans from which these samples were taken? (Gordon)

5. On March 30, 1966, the Anton Brun found an area of upwelling off PTA S. Nicolus on the west coast of Peru. At a depth of 10 m the water contained 2.91 ml O_2/liter. The temperature was 15.84C and S $^{o}/_{oo}$ = 34.889. What was the percent saturation of oxygen compared to a water vapor saturated atmosphere at 760 mm pressure.

After setting a droug and following the upwelled water mass as it flowed north for four days a sample taken at 10 m contained 6.05 ml O_2/liter. The temperature was 16.04C and salinity = 34.855. What was the percent saturation of oxygen now? (Loder)

6. Where did the molecular oxygen of the oceans and atmosphere come from? What impact does its presence have upon the marine chemistry of nitrogen? (Gordon)

7. At point A in a particular location in the sea the surrounding dissolved oxygen field is uniform except for an increase at a constant rate of 0.20 ml/l/km in going from west to east. A current is setting north at 0.30 m/s and the dissolved oxygen concentration at point A is decreasing by 1.5×10^{-5} ml/l/s. Show, diagram, write the applicable equation, and give the following:
(a) local change (b) rate of change due to advection (c) rate of change due to biochemical-biological processes (d) rate of change due to diffusion (e) individual change (f) what change in ambient oxygen concentration would be experienced by a fish swimming east at 0.50 km/hr. (Baier)

8. Compare, by drawing sections, the oxygen distributions in the Atlantic and Pacific Oceans. In your comparison be sure to (a) identify major similarities and differences and give reasons for the similarities and differences, (b) identify sinks and replenishment areas, and (c) give reasons for areas of high apparent oxygen utilization. (In your sections, use either percent saturation or absolute concentration units for O_2). (Duedall)

9. (a) Describe the O_2 distribution associated with the following water masses and where the water masses are formed: (1) Antarctic Intermediate (2) North Atlantic Deep (3) North Pacific Intermediate (4) Antarctic Bottom Water

(b) Explain briefly how Antarctic Intermediate Water is formed. (Duedall)

10. If 1.25 moles of oxygen are needed to consume each mole of particulate carbon tissue, what must the $[O_2]$ concentration in surface water be to prevent the deep ocean from going anaerobic? Dissolved $[O_2] = \alpha[PO_2]$ where PO_2 = 0.2 atm, α = 1.5 mmol/(atm (at 35 $^{o}/_{oo}$, 0C). If the $PO_4^{=}$ of the deep ocean increases by a factor of 2, what happens? If the icecaps disappear and deep water is produced at 20C (where α = 1.1 mmol/(atm), what happens? (Hammond)

11. Explain why 'apparent oxygen utilization' values for surface waters may be anomalous in certain parts of the world ocean. (Duedall)

12. A sample of deep water from the Pacific Ocean has the following gas content: N_2 = 12.91 ml/L, O_2 = 7.26 ml/L. The pertinent Bunsen coefficients are: N_2 = 0.0165, O_2 = 0.0346 (units are ml/ml). The atmosphere contains: 78.08% N_2, 20.94% O_2. Calculate the apparent oxygen utilization. Knowing that the deep Pacific has high concentrations of phosphate, presumably of oxidative origin, do you believe the result? (Keeburgh)

13. In the absence of $[O_2]$, $SO_4^=$ can be used as an oxygen source for the oxidation of tissue by bacteria. We might expect to see nutrients co-vary as they do in the Redfield AOU model. At oceanic pH, the reaction for complete tissue breakdown could be written:

$$C_{100}N_{15}P + 124H_2O + 2H_2CO_3 + 45SO_4^= \longrightarrow 102HCO_3^- + 45H_2S + 15NH_4^+ + PO_4^=$$

What slopes would be observed for the following plots (you may write them as whole number ratios)?

(a) ΣCO_2 vs. PO_4 (i.e., $\Delta\Sigma CO_2/\Delta PO_4$)

(b) ΣCO_2 vs. H_2S

(c) NH_4^+ vs. $PO_4^=$

(d) Is there any alkalinity change? Why (briefly)?

(Hammond)

14. Describe the chemical processes (you needn't balance the equations) during organic decomposition (i.e. plankton) by which a system becomes anoxic. List the hydrogen acceptors and the sequence which they are utilized in these reactions or processes. (Adams)

15. Mediterranean Water enters the Atlantic Ocean with a temperature of 11.9C and a chlorinity of 20 °/oo. It mixes with North Atlantic Deep Water which is characterized by a temperature of 2.8C and a chlorinity of 19 °/oo. If one were to use A.O.U. to study the mixing of these two water types what would be the error in A.O.U. due to the nonlinearity in O_2' when a 50%-50% mixture was reached? The vapor pressure of Mediterranean Water is 10.3 mm of Hg; for North Atlantic Deep Water it is 5.57 mm of Hg; it is 7.50 mm of Hg for the 50-50 mixture. You may assume a constant atmospheric pressure of 760 mm of Hg for this calculation and a relative humidity of 100% at equilibrium. (Kester)

16. Given two water masses: Mass A: Salinity = 30 °/oo, Temp. = 10C; Mass B: Salinity = 35 °/oo, Temp. = 26.7C. Assume that each mass was saturated with air at 760 mm pressure when the water was at the surface. Mix equal portions of each water mass and ignore the small density change. How has the percent saturation of nitrogen gas changed and by how much? (If necessary vapor pressure of water is 9.2 mm at 10C and 26.3 mm at 26.7C). (Loder).

17. A large volume of gas contains N_2, O_2, Ar and water vapor. The partial pressures of N_2 and Ar are 577 and 7 mm of Hg, respectively. Its relative humidity is 50% and the vapor pressure of liquid water is 24 mm of Hg. This gas mixture is at atmospheric pressure which according to a barometer is 740 mm of Hg. When a small amount of seawater is placed in contact with this gas mixture it equilibrates reaching a final concentration of 6.50 ml O_2/l. What is the Bunsen constant of O_2 in seawater under these conditions? (Meyers)

18. The solubility of N_2 per atmosphere of N_2 gas pressure is 0.80 moles/m^3 at 0C. What is the solubility of N_2 in surface waters which are at equilibrium with the atmosphere whose P_{N_2} = 0.781 atm. (Duedall)

19. A sample of seawater of 35 $^{o}/_{oo}$ salinity at 10C contains nitrogen and oxygen as its only dissolved gases. This seawater is placed in a closed container with no air or any gases other than the N_2 and O_2. The pressure on the seawater is reduced to 300 mm of Hg and a gaseous phase form. After a period of time the gas phase and the seawater reach equilibrium. A Winkler analysis shows that the seawater now contains 3.20 ml of O_2/l. What is the concentration of N_2 in the seawater? You will need the following information: at 300 mm of Hg pressure, 10C, and 35 $^{o}/_{oo}$ salinity the Henry's Law constants are: $^{a}O_2$ = 0.0402 ml l^{-1} (mm of Hg)$^{-1}$; $^{a}N_2$ = 0.0195 ml l^{-1} (mm of Hg)$^{-1}$. The vapor pressure of seawater is 9.04 mm of Hg. The relative humidity of the gas phase is 100%. (Kester)

20. The atmosphere contains 78% nitrogen and 21% oxygen. The ratio of nitrogen in the atmosphere is almost 4:1, while the same ratio in the ocean is almost 2:1. Why? (Reeburgh)

21. It has long been known that nitrogen saturation over 110% is lethal for fish (Marsh and Gorham, 1904). Using available solubility data determine the maximum rate that heat from an atomic reactor could be dumped into a tide-mixed estuary in winter given the following data:

    Average low tide depth = 3 m — Average winter temp. = 10C (at S $^{o}/_{oo}$ = 32)

    Average low tide width = 100 m — Nitrogen content of water in winter = 90% of saturation

    Average low tide length = 10 km — Specific heat of seawater = 0.96 cal/g/^{o}C

    Tidal volume = 10^6 m^3

    State all assumptions and discuss briefly the restraints which should be placed on the operation of such a reactor. (Baier)

22. Discuss the application of dissolved rare gases in the sea to problems in oceanography. (Ku)

23. List several reasons which might invalidate data on gas concentrations in a parcel of water (let's say collected from 3000 m), where these values were determined from the in situ S $^{o}/_{oo}$ and temperature. (Adams)

24. What differences in the surface concentrations of inert gases would you expect between high latitudes and low latitudes? Explain the reasons for your answer. (Gordon)

25. Explain Bieri's (The Sea, v. 5) interpretation of the Ne, Ar, and He anomalies in the ocean. In your discussion be quantitative by giving the size of the anomaly for each gas and also indicate to what factor(s) these anomalies are sensitive. (Duedall)

26. Assume that someone proposed to approach the problem of "excess He" in the ocean by obtaining measurements of the $^{3}He/^{4}He$ ratio in seawater.

    (a) What unique factor might make this approach attractable?

    (b) What factor(s) might make this approach difficult? (Duedall)

27. Given the following information:

	ΔG^0, Kcal
$NH_3 \cdot H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	6.5
$NH_{3(g)} + H_2O(l) \rightleftharpoons NH_3 \cdot H_2O(l)$	-2.4

$[NH_4^+] = 2 \times 10^{-6}M$

pH of seawater = 8.2

(a) What is the equilibrium concentration of NH_3 gas in the atmosphere, relative to the reactions above?

(b) If the NH_3 gas concentration in the atmosphere over the ocean is 3 $\mu g/m^3$, would the sea be a source or a sink for NH_3, according to the above. (Duce)

3. *Carbon dioxide and related principles*

a. pH, alkalinity

1. What is pH? How is it measured, how is it defined, and what do the measurements represent? What effect do junction potentials have on seawater pH measurements and how can they be avoided? (Reeburgh)

2. Calculate the pH of a water droplet in equilibrium with atmospheric CO_2, SO_2, and NH_3. Use the following information:

Equilibrium Constants

$H_2O \rightleftharpoons H^+ + OH^-$	$K_W = 1.01 \times 10^{-14}$	$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$	$K_{1A} = 1.77 \times 10^{-5}$
$(SO_2)_g + H_2O \rightleftharpoons SO_2 \cdot H_2O$	$K_{HS} = 1.24$	$(CO_2)_g + H_2O \rightleftharpoons CO_2 \cdot H_2O$	$K_{HC} = 3.4 \times 10^{-2}$
$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$	$K_{1S} = 1.27 \times 10^{-2}$	$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$	$K_{1C} = 4.45 \times 10^{-7}$
$HSO_3^- \rightleftharpoons H^+ + SO_3$	$K_{2S} = 6.24 \times 10^{-8}$	$HCO_3^- \rightleftharpoons H^+ + CO_3^=$	$K_{2C} = 4.68 \times 10^{-11}$
$(NH_3)_g + H_2O \rightleftharpoons NH_3 \cdot H_2O$	$K_{HA} = 57$		

Atmospheric Concentrations

$(NH_3)_g = 2.0\ \mu g/m^3$ (STP) $\qquad (SO_2)_g = 1.1\ \mu g/m^3$ (STP) $\qquad (CO_2)_g = 311$ ppm (STP)

(Duce)

3. Shortly after ascending to office, President Ford was rumored to have said he thought the Arab oil embargo would soon end because the Arabs needed the money. Although Press Secretary Ziegler denied the statement and called it inoperative, the Arab nations took strong offense. In a protest, that got slightly out of hand, all of the stored oil was burned. The stockpiles were so vast that this sudden burning of fossil fuels has led to a doubling of the CO_2 in the atmosphere (now 630 ppm CO_2). This new concentration appears to be world wide and to be stable. What is the resultant pH and carbonate alkalinity of the sea? Assume the sea to be of 19 °/oo chlorinity at 20C but with the ionic strength dependent only upon Na^+ and Cl^- ions (0.6 m in NaCl). Values for the Debye-Huckel expression:

$A = 0.5042$ $\qquad {}^{o}_{a}Ca^{++} = 6.0 \times 10^{8}$

$B = 0.3273 \times 10^{-8}$ $\qquad {}^{o}_{a}H^{+} = 9.0 \times 10^{8}$

${}^{o}_{a}HCO_3^- = 4.0 \times 10^{8}$ $\qquad {}^{o}_{a}OH^- = 3.5 \times 10^{8}$

${}^{o}_{a}CO_3 = 4.5 \times 10^{8}$

Use the apparent dissociation constants of carbonic acid for 20C and 19% chlorinity of: $pK_1 = 6.02$, $pK_2 = 9.17$. Assume that the water is saturated in respect to $CaCO_3$ and ignore borate, silicate buffering, and ion pairing. (Sharp)

4. What pH change would be expected if 1 mg of organic carbon in a liter of seawater were completely oxidized? Use: $C_{CO_3^{2-}} = 0.0002$ moles/l; $C_{HCO_3^-} = 0.001$ moles/l. What assumptions are necessary? How far beyond the visible end point of a Mohr titration would one go to precipitate Ag_2CO_3 from the above oxidized seawater? Assume the visible end point was established with 6 drops of a saturated solution of K_2CrO_4 (0.015 M in 40 cc of titrated sample). (Baier)

	K_{sp}		K_{sp}		K_{sp}
AgCl	2.8×10^{-10}	Ag_2CrO_4	1.9×10^{-12}	K_2CrO_4	27
AgBr	5×10^{-13}	Ag_2CO_3	8.2×10^{-12}	$K_2Cr_2O_7$	1/27
AgI	8.5×10^{-17}	AgF	14	$Ag_2Cr_2O_7$	2×10^{-7}

5. Consider a one liter sample of Sargasso seawater having 36.5 °/oo salinity at atmospheric pressure and 23C. Its pH is 8.20 and its specific alkalinity is 0.123 meq/l/°/oo. This seawater is placed in a closed vessel containing some zooplankton and $CaCO_3$ sediment. After a period of time the zooplankton have consumed 5.0 ml of O_2 and 0.050 g of $CaCO_3$ have dissolved. What is the final pH? (Kester)

6. Show that the pH of a seawater sample can be derived from the knowledge of its total alkalinity and total dissolved CO_2 (ΣCO_2). (Ku)

7. Distinguish between total alkalinity and carbonate alkalinity. What processes cause their changes in the ocean? How do their values relate to that of ΣCO_2? (Duedall)

8. What is the pH of maximum bicarbonate (HCO_3^-) concentrations in seawater at a temperature of 3C and a salinity of 32.5 °/oo? (Loder)

9. What are the percentages of H_2CO_3, HCO_3^-, and CO_3^{-2} in our coastal waters at a temperature of 3C, a salinity of 32.5 °/oo and a pH of 8.00? (Broad hint department--use Henderson-Hasselbalch Equation.) (Loder)

10. What would the borate alkalinity be in the seawater sample with temperature = 3C, S °/oo = 32.5 °/oo, and pH = 8.0? (Loder)

11. The alkalinity of the surface ocean is 2.0×10^{-3} meq/l, and pH ≈ 8.15. Calculate the oceanic p_{CO_2} for $\alpha^{25^\circ} = 0.030$ mol/ℓ-atm, $K_1' = 1 \times 10^{-6}$, $K_2' = 8 \times 10^{-10}$ and compare this to the atmospheric value $\alpha^{15^\circ} = 0.04$ mol/ℓ-atm, but the other constants are less sensitive to temperature. Calculate p_{CO_2} of the surface ocean at 15C. (Hammond)

12. The surface ocean has a carbonate alkalinity ($HCO_3^- + 2\,CO_3^=$) of 2.0 meq/l and a pH of 8.15. Calculate the oceanic p_{CO_2} at 15C and 25C. You will find the following constants helpful:

	15C	25C	
α, mmol/l atm	40	30	Salinity = 35 °/oo
K_1'	0.9×10^{-6}	1.0×10^{-6}	
K_2'	0.6×10^{-9}	0.8×10^{-9}	

If the sea surface was warmed by 10C, what effect would this have on atmospheric composition? (Hammond)

13. Why does alkalinity increase in deep ocean water? Give evidence to support your reason. (Reeburgh)

14. A sample of seawater is obtained from a depth of 4500 m where the temperature is 2.50C; its salinity is 34.90 °/oo. On board ship the pH of this sample is 7.65 at 25C, 1 atm pressure and its total alkalinity is 2.40 meq $(kg\ H_2O)^{-1}$.

    (a) Calculate the in situ pH of this sample.

    (b) Calculate the carbonate alkalinity at in situ conditions.

    (c) Derive a relationship between ΣCO_2 and CA in terms of K_1', K_2', and a_H.

    (d) Calculate ΣCO_2, P_{CO_2}, and m_{CO_3} for the in situ water. (Kester)

15. Does the alkalinity of seawater (isolated from its surroundings) increase (a); decrease (b); or (c) stay constant upon addition of small quantities of the following salts or neutral molecules? N_2, HCl, KOH, K_2CO_3, $KHCO_3$, $NaHCO_3$, H_2CO_3, CO_2, Na_2SO_4, K_2SO_4, Na_2HPO_4, Na_2SiO_3, K_3PO_4, $CaCO_3$, SO_2, Na_2CO_3, CS_2. Indicate the relative increase or decrease in alkalinity per mole of compound added. (Example: $CaCO_3$ - 2 alkalinity units per mole added). (Duedall)

16. Explain how the alkalinity and pH respond when we do the following things to seawater: (a) add river water? (b) remove carbon dioxide, but do not precipitate carbonates? (c) warm the water? (d) subject the water to high pressures? (e) expose the water to a plankton bloom? (f) add ammonia and carbon dioxide in an anoxic basin? (g) precipitate carbonates? (Reeburgh)

17. What is the maximum contribution in milliequivalents per liter of the orthosilicic acid (H_4SiO_4) system to the alkalinity of seawater? Use 200 µM as the maximum concentration of total dissolved inorganic silicate (total orthosilicic acid plus orthosilicate ions), pH = 8.0, pK_1' of H_4SiO_4 = 9.3. (Gordon)

18. What percent of boric acid would be present as the undissociated molecule and as the monoionized anion at a depth of 2026 m for water 19.5 °/oo Cl and 5.0C if the pH measured at one atmosphere pressure were 7.92? What would the in situ borate alkalinity of this water be? (Hulbert)

19. One sunny day in mid-July whilst on Appledore Island in the sun-dappled Isle of Shoals, a very clever student, Greta Grad, was given the following simple assignment:

    Find a medium-sized tidal pool on Appledore with plenty of algae and monitor the pH change during the day. Greta decided to also measure the dissolved oxygen, temperature and salinity. She had a nice fancy digital portable pH meter to measure the pH, oxygen bottles and reagents for dissolved oxygen, bottles for salinity, a thermometer, and a good book to read. She found a pool that was left by the falling tide two hours before low tide giving her a little over four hours to monitor the changes. She decided to take only two readings, one at the start and one just before the pool started to refill.

    She found the pool was at 17.5C and the pH was 8.17. She took dissolved oxygen and salinity samples. After four hours of reading and eating lunch, she made the final readings. The temperature had risen to 25C, and she collected the oxygen and salinity sample bottles. As she prepared to take the pH reading, an angry gull dive-bombed her and alas and alack she dropped the pH electrode (it broke)! Since the tide was rising and the assignment was due the next morning, she couldn't redo the experiment. However, by assuming that the specific alkalinity for the water was 0.123 she was able to use the following data she collected to calculate the pH change.

Tidal Pool Start:		The Finish:	
0930 hours	Temp. = 17.5C	1330 hours	Temp. = 25C
	Sal. = 32.5 °/oo		Sal. = 32.5 °/oo
	Diss. O_2 = 5.49 ml/l		Diss. O_2 = 9.24 ml/l
	pH = 8.17		pH = ?

Greta assumed that oxygen produced during photosynthesis was not lost while she watched the pool. How did Greta save the assignment and impress the professor? What was the final pH of the pool? Remember that photosynthesis takes up CO_2 which will cause the pH to change, but there is no change in total alkalinity. You should need the solution to the quadratic equation. (Loder)

b. Carbon dioxide equilibrium and distribution

1. (a) Define Total CO_2 (TCO_2).
   (b) Define carbonate alkalinity (C.A.)
   (c) Roughly, under what pH conditions would TCO_2 be greater than C.A.?
   (d) What might cause this?
   (e) Is this a typical situation in the oceans? Why? (Gordon)

2. Under what conditions will the "total CO_2" in seawater be higher than the carbonate alkalinity and under what conditions will it be less? (Gordon)

3. Explain why the solubility of CO_2 in seawater (with 1 atm of CO_2 above the liquid and total P = 1 atm) is orders of magnitude greater than the solubility of other gases with partial pressures equal to 1 atm. (Duedall)

4. What arguments can be advanced to explain that the rate of gas exchange across the sea's surface for CO_2 is not necessarily perturbed by the hydration behavior of the gas. (Cooke)

5. According to Broecker "throughout the ocean, the following chemical reaction is continually taking place": $H_2O + CO_2 + CO_3^{-2} = 2HCO_3^-$. This reaction can also be written as $2HCO_3^- = CO_3^{2-} + CO_2 + H_2O$ or $2HCO_3^- = CO_3^{2-} + H_2CO_3$. By considering the following reactions, show that the equilibrium constant for $2HCO_3^- = CO_3^{2-} + H_2CO_3$ is given by K_2/K_1. (Duedall)

$$H_2O = H^+ + OH^- \quad , K_w \qquad HCO_3^- = H^+ + CO_3^{2-} \quad , K_2$$

$$H_2CO_3 = HCO_3^- + H^+ \quad , K_1 \qquad HCO_3 + H_2O = H_2CO_3 + OH^- \quad , K_h$$

6. Write an expression for the thermodynamic equilibrium constant K_2 for the reaction $HCO_3^- = H^+ + CO_3^=$. On what 2 variables does K_2 depend? Write an expression for the "apparent" equilibrium constant K_2'. On what variables does it depend in seawater? (Hammond)

7. Assume you were not aware of apparent dissociation constants for carbonic acid and you calculated the C_{HCO_3} of a seawater solution whose pH = 8 using K values for distilled water. What error would result in your calculation? Assume $C_{CO_3^{2-}}$ equal 0.1 x $C_{HCO_3^-}$, and the salinity to be 35 °/oo and temperature to be 20C. $pK'_1 = 6.02$ and $pK'_2 = 9.17$. You can use the following thermodynamic constants for carbonic acid in distilled water: $K_1 = 4.4 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. (Duedall)

8. Consider definition of a constant ionic medium scale for equilibrium constants for use in marine chemistry based upon aqueous 0.70 M NaCl. Why is this solution an apt choice for definition of the constant ionic medium? What deficiencies has it? For the $CO_2/H_2CO_3/HCO_3^-/CO_3^=$ system, what would cause the equilibrium constants based on concentrations (e.g., $K_{2,c} = [CO_3^=][H^+]/[HCO_3^-]$, where $[CO_3^=]$ = concentration of free $CO_3^=$, etc.) in the 0.70 M NaCl to differ from those in seawater? (Hulbert)

9. A certain seawater has a carbonate alkalinity of 2.4 meq/l and a "total CO_2" of 2.2 mM. Calculate the new carbonate alkalinity and total CO_2 if the following occur (always such that no material can enter or leave the water other than what we specify):
   (a) 0.1 millimole of $CaCO_3$ dissolves in one liter of the water.
   (b) A submarine volcano injects 0.1 millimole per liter of HCl.
   (c) Marine plants remove 0.1 millimole per liter of CO_2.
   (d) If you have time, after finishing the rest of the question, consider (a), above, plus the addition of 0.1 millimole of CO_2 by decomposition of organic matter. Calculate the combined effect. (Gordon)

10. During a pleasant summer cruise a mythical student collected a surface sample and found a Cl $^0/_{00}$ = 18.0 and a specific alkalinity = 0.123. The water was 20C and had a pH of 8.2. After these determinations our student analyst took a break for dinner and a couple rounds of cribbage. He lost and had to return to the lab and determine the amount of CO_2 lost during the time he was losing.

    He found that the temperature of the sample was now 26C and the pH had risen to 8.6. Assuming the sample was in equilibrium with the atmosphere, what was the CO_2 loss because of this change? In addition, what was the change in the concentration of H^+ ion? (Loder)

11. Consider a parcel of water at the surface in some source area in the Southern Ocean. Describe the changes, and those processes affecting the changes, in the gas composition as the parcel sinks and moves in a northerly direction. Please contrast the reactive and unreactive gases. (Duedall)

12. List those physical, biological, atmospheric, and chemical processes which maintain the high pCO_2 in the equatorial region of the Pacific Ocean and the low pCO_2 in the Central Pacific. (Duedall)

13. Assume a sample of North Atlantic Deep Water has a temperature and salinity such that its O_2 (sat) under *in situ* conditions is 0.38 μM. Calculate the increase in TCO_2 assuming that this wonderful water mass did not mix with any other types since its formation, and that no alkalinity changes occurred. Please note that in order to solve this problem you will have to make some assumption about the concentration or percent saturation of O_2 in the North Atlantic Deep Water. (Duedall)

14. Sketch a CO_2 profile for the ocean. Why is the ΣCO_2 high in the Pacific surface waters compared to the atmosphere? (Millero)

15. If the ΣCO_2 of the deep ocean is about 2.3 mmol/l and the atmosphere is about 330 ppm CO_2 by volume, calculate the ratio of CO_2 in the ocean to that in the atmosphere per cm^2 of earth surface. (Hammond)

16. Seawater is able to serve as a sink for fossil fuel CO_2 because of the reaction $CO_2 + H_2O + CO_3^{=} \rightarrow 2HCO_3^{-}$.

(a) Does this reaction change the alkalinity of seawater?

(b) If fossil fuel burning continues adding CO_2 to the ocean, will the compensation level fall or rise? Explain your reasoning.

(c) What 3 time constants are involved in changing the compensation level by burning fossil fuel? (Hammond)

17. If we assume that all CO_2 produced by fossil fuel combustion remains in the atmosphere:

(a) calculate the fraction of today's CO_2 produced since the beginning of the industrial revolution.

(b) calculate the CO_2 fraction when all fossil fuel is exhausted.

(c) calculate the fraction of atmospheric oxygen required to burn all fossil fuels. Atm. mass = 5×10^{21} g, mean M.W. = 29. (Hammond)

gas	N_2	O_2	A	CO_2
fraction by volume	0.78	0.21	0.01	0.00033

Fossil Fuel (as gms of carbon)	Initial total	Fraction used (1973)
Coal reserves (mineable)	7.6×10^{18}	3%
Oil reserves	2.3×10^{17}	20% (approx)

18. Man can easily tolerate atmospheric pressure variations of 30%. Do you believe fossil fuel burning can ever seriously affect the atmospheric oxygen reservoir? (Hammond)

19. Fossil fuel consumption is releasing large amounts of CO_2 to the atmosphere, but much of this can be taken up by the oceans or incorporated as plant tissue. Cite 2 arguments that some of this CO_2 remains in the atmosphere (i.e., that the CO_2 content of the atmosphere is increasing). (Hammond)

20. You have available a gas counter suitable for determining C^{14} activity, with a stable background of 1.5 counts per minute. Careful determinations of the specific activity of modern wood (grown between 1935 and 1940) yield 13.7 1.4 dpm/gC. You prepare a suitable counting gas containing 5.0 g of carbon from ocean sediment sample whose age you wish to determine and fill the counter with this gas. A 3,000 minute count yields 54,183 observed decay events.

Assume (1) that your counting efficiency is 100%. (2) that the Suess effect is negligible. (3) that the half life of C^{14} is 5730 ± 30 yrs. (4) that isotopic fractionation effects may safely be neglected.

Calculate: (1) the C^{14} "age" of the sample. (2) What additional assumption must be made if the above "age" is to be interpreted as a true age? (3) Justify assumption 1, 2, and 4 above if possible. (Kroopnick)

c. *Carbonates*

1. Sketch a profile of the degree of saturation of calcite in seawater. How and why is such a profile different for the Atlantic and Pacific oceans? (Millero)

2. (a) Distinguish between the calcium carbonate compensation depth and the lysocline.
(b) How will they be affected if the concentration of carbon dioxide in the atmosphere increases markedly, say by combustion of large amounts of coal and petroleum?
(c) What magnitude of time scales would you assign to these effects? Justify your answer. (Gordon)

3. Describe the chemical process occurring when
(a) CO_2 is bubbled through seawater (b) a hurricane diverts cold deep water past $CaCO_3$ deposits. (c) A $CaCO_3$ shell falls to the bottom of the Mariana Trench (d) Surface layers supersaturated with $CaCO_3$ are heated by solar radiation. (Baier)

4. Explain the observation that the so-called "compensation depth" for $CaCO_3$ in the Pacific is shallower than in the Atlantic. (Ku)

5. A seawater sample of temperature 20C and salinity of 35 $^0/_{00}$ has a pH of 8.0 and a carbonate alkalinity of 2.4 meq/l. Is this seawater saturated, oversaturated, or undersaturated with respect to $CaCO_3$? Show your calculations. (Gordon)

6. (a) Only about 9% of the carbonate ion in seawater exists as such. In what other forms does it exist and to what extent in each?
(b) In what forms does magnesium ion exist in seawater and to what extent? (Gordon)

7. Is the surface ocean saturated or undersaturated with calcite? [$K'_{sp} = 1 \times 10^{-6}$ for $CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{=}$ and $[Ca^{++}] = 1 \times 10^{-2}$ mol/l]. (Hammond)

8. Calcium carbonate solubility increases with increasing pressure (all else constant). The CRC handbook lists calcite as hexagonal with specific gravity of 2.711 and aragonite as rhombohedral with specific gravity of 2.93. Which of the two forms will be more sensitive to change in pressure and why? (Hint: What causes changes in solubility with changes in pressure?) (Hulbert)

9. By what mechanisms might the following marine deposits have accumulated? Be brief.
(a) An earthy deposit containing unusually large amounts of Na_2SO_4. (b) Intermixed layers of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$. (c) Intermixed layers of $CaCO_3$, $CaSO_4 \cdot 2H_2O$, and NaCl. (d) Relatively pure $CaCO_3$. (Gordon)

10. Approximately 50% of the ocean floor lies above the compensation level. Assuming that forams fall straight down, that productivity is uniform in the surface ocean, and that no solution of $CaCO_3$ occurs above the compensation level, what fraction of shells produced survive destruction? Calculate the accumulation rate of $CaCO_3$ above the compensation level in cm/10^3 yrs. [Assume $\rho_{CaCO_3} = 2.5$ gm/cm^3, MW = 100.] (Hammond)

11. The variation of the equilibrium constant with pressure is $\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^0}{RT}$, where V^0 is the standard partial molar volume.
(a) Assuming that ΔV^0 is independent of pressure, calculate the effect of depth on the solubility product constant of calcium carbonate.

(b) Assume that the oceans are uniformly mixed and that the concentrations of Ca^{+2}, ΣCO_2, and alkalinity are: Ca^{+2} = 0.41 g/kg seawater, $\Sigma CO_2 = 2.25 \cdot 10^{-3}$ M/kg seawater, Carbonate alkalinity = $2.3 \cdot 10^{-3}$ eq/kg seawater. Calculate the depth at which the ocean becomes undersaturated with respect to calcium carbonate (i.e. when a foraminifera shell should begin to dissolve).

(c) Will it really dissolve?

(d) What implications does this have on the distribution of carbonate sediments in the oceans?

(Kroopnick)

		V^o cm^3 $mole^{-1}$ (25C)	
$Sr = Sr^{+2} + 2e$	+2.89	$CaCO_3$	36.9
$1/2\ H_2 = H^+ + e$	0.00	Ca^{+2}	-17.7
$Cu = Cu^{+2} + 2e$	- .337	$CO_3^=$	-3.7
$NO + 2H_2O = NO_3^- + 4H^+ + 3e$	- .96		
$2Cl^- = Cl_2 + 2e$	-1.36		

R = gas constant = 1.987 Cal $mole^{-1}$ $degree^{-1}$ = 80.06 cm^3 atm $mole^{-1}$ $degree^{-1}$

1 atm = 1.013 bar

12. If a core from a 4000 m depth is found to have an interstitial water pH = 7.5 and is in equilibrium with calcite, what is the P_{CO_2} at 26C, 1 atm? (Morse)

13. Assume a 2-layer ocean. In the upper layer the temperature changes from 30C to 0C over a small depth range so that the effect of P on G can be neglected. In the lower layer T is constant at 0C. At what depth would calcite become unstable with respect to aragonite? Given. (Assume α and β T indep.)

	Calcite	Aragonite	
ΔG_f^o	-269,780	-269,530	cal
V	36.94	34.16	cm^3/mole
α	1.58×10^{-5}	5.55×10^{-5}	deg^{-1}
β	1.37×10^{-6}	1.55×10^{-6}	atm^{-1}
ΔH_f^o	-288,086	-288,134	cal
Cp	$24.98 + (5.24 \times 10^{-3}\ T) - (6.20 \times 10^{5}\ T^{-2})$	$20.13 + (10.24 \times 10^{-3}\ T) - (3.34 \times 10^{5}\ T^{-2})$	(Morse)

14. A student added some phenolphthalein indicator to seawater and observed that the solution was colorless. (Phenolphthalein changes from colorless to pink as pH goes from 8.2 to 10.0.) He then bubbled pure nitrogen gas through the seawater and very soon the indicator turned pink. After somewhat longer he observed that a white precipitate formed. Explain what happened using chemical equations. (Gordon)

D. Nutrients

1. Analytical methods

1. In the determination of phosphate in the water from the open ocean, you did not correct for arsenate contamination, yet arsenate will interfere with the reactions of the method. Why did you do this? (Adams)

2. In the determination of phosphates, what happens if the concentration of hydrogen ion in the mixed reagent (containing molybdate, etc.) is insufficient? Is too great? (Adams)

3. In the nitrate determination, what prevents the buildup of cadmium hydroxide coating on the surface of the amalgam? If this had not been done, what would the effect be on the final concentration of nitrate that you are measuring? (Adams)

4. In the phosphate analysis, what chemical is used to reduce the phosphomolybdate complex? Why isn't the silicomolybdate complex reduced by this agent? (Baier)

5. In passing the water samples through the reduction columns for the determination of nitrate, why must the flow rate be precisely regulated? (Adams)

6. Suppose you are in charge of running phosphates on an Eastward cruise and the wavelength dispersion prism of your D.U. comes loose from its turning shaft. Being a clever student you cement the prism to the shaft with epoxy and realize now that the wavelength scale is out of calibration. What procedure would you follow to set the prism for the proper wavelength? (Baier)

7. H.W. Harvey, in his book The Chemistry and Fertility of Sea Waters, p. 141, gives the concentration of phosphorus as phosphate-phosphorus in the oceans as <1 - 60 (mg per m^3) = (µg per liter). To what concentration in units of (µmol per kg) does the 60 (mg per m^3) correspond? Assume a density for his seawater of 1.03. (Gordon)

2. Distributions and relationships

1. Write equations for the oxidative contributions of N and P. (Please be careful of units and carefully define any terms and their units.)
   (a) N_{ox} = (b) P_{ox} = (Duedall)

2. Explain the principal limitation in using the preformed nutrient concept. (You may wish to derive some equations based on the Redfield model.) (Duedall)

3. What measurements are required to be made on a seawater sample in order to estimate its preformed phosphate content? Show specifically how each is used. (Gordon)

4. At a site being considered for culture of clams, the seawater which supplied the region was found to have a total phosphate concentration of 0.5 μmol/kg while the nitrate concentration was 20 μmol/kg. The clams involved were filter feeders, whose food source was to be phytoplankton grown in this same seawater. Would you recommend fertilizing this water? If so, why, with what, and how much? (Gordon)

5. A seawater sample was taken at a depth of 900 meters. Its salinity was 35.0 °/oo, its oxygen concentration was 3.36 ml/L, and the inorganic phosphate was 1.60 μg-at/L. The equilibrium solubility of oxygen in this water sample was found from tables to be 5.60 ml/L.
   (a) What is the concentration of preformed phosphate in this water sample?
   (b) What would you expect the concentration of total and preformed nitrate to be, if in this case it can be assumed that the nitrate-phosphate concentration ratio equals the ratio of change?
   (c) From which ocean would you expect this water sample to be derived? (Baier)

6. When the following phosphate data is plotted versus depth, the figure shows some interesting reversals in the phosphate concentrations of surface water. Give one possible explanation for this reversal. What is the ecological significance of such a mechanism? Data: 0 m, 49 μM P; 10 m, 44 μM P; 20 m, 38 μM P; 30 m, 43 μM P; 40 m, 50 μM P; 50 m, 100 μM P. (Bear Cruise #185, sta #260, 40°43.7'N, 71°41.0'W, May 13, 1958). (Duedall)

7. (a) Why are the plant nutrient concentrations generally low in surface waters and high in deep waters?
   (b) Why doesn't this result affect the salinity distribution of the oceans? Or, does it? Defend your answer. (Gordon)

8. Why does nitrite, when it occurs in the water column, typically occur in a thin layer just overlying the rapid increase with depth of nitrate? (Gordon)

9. Describe a hypothetical vertical profile for each of the following: Give the range of concentrations expected for each at the given location and worldwide.
   (a) reactive phosphate in the N. Pacific (b) dissolved oxygen in the Antarctic (c) silica in the Peru current area. (Kroopnick)

10. Nutrients take part in a continuous cycle in which they are fixed, dispersed, and regenerated. Describe these processes in more detail using either phosphorus, nitrogen or silica as an example. Have I left out any steps? If so, which? (Kroopnick)

11. (a) Briefly describe and discuss the model Richards has proposed to describe biological production and degradation of organic matter in the oceans. (b) Use this model to calculate the percentage effect of consuming all the dissolved oxygen in a water (initially containing 6.18 ml/liter) upon the total CO_2 of the water, assuming a typical total CO_2 value for seawater. (c) Use the model to calculate enough values of preformed phosphate so that you can sketch in a curve of preformed phosphate versus depth on your phosphate plot for NH-65 and hand it in with this question. Identify the curves or areas which represent the various phosphate fractions. (d) Which phosphate fraction appears to be most useful in physical oceanographic studies? Briefly, why? (e) Which phosphate fraction or fractions appear to be most useful in biological studies? Why?--again, be brief. (Gordon)

12. (a) Describe the nitrogen cycles in the ocean. (b) How do they differ, if at all, from the phosphorus cycles? (c) Show how, on a rough graph, nitrogen (abscissa) varies with phosphorus (ordinate) in the open oceans. What is the slope of the curve? How do you know? What is the intercept, in a qualitative sense only? How do you know? (d) Draw a vertical section of nitrate distribution with the section perpendicular to a coastline and during a period of active coastal upwelling such as we find along the Oregon coast. Try to put some typical numbers on the isopleths. (e) Ammonia figures in the nitrogen cycle. It is also a weak base. Why do we not consider ammonia as a part of the alkalinity of seawater? (Gordon)

13. The so-called "Richards" or "Redfield, Ketchum, and Richards" model relates changes in carbon dioxide, oxygen, nitrate, and phosphate concentrations in the oceans to the formation or degradation of organic matter of a "statistical average" composition.
(a) Write the chemical equation for this model. (b) On what basis is this model founded? (c) How will this model change if the principal inorganic nitrogen source and sink becomes NH_3 instead of HNO_3? Write the new equation. (d) Does this situation ever occur in the oceans? Where and how? (e) How does this model change in a situation like a restricted basin which has nearly normal surface waters (aerobic, reasonable nutrient supplies, well lit by sunlight) but zero oxygen concentrations in its deep waters? (Gordon)

14. Assume the change in the concentration of P in a local bay is 0.01 μM over a 4 hour period. Calculate the expected change in nitrogen (over the same time period) based on the Redfield model. Please list any assumption(s) you feel have to be made based on the information available. (Duedall)

15. Discuss, using outline form if you wish, the distributions of oxygen, phosphorus and nitrate which you would expect to find in the Atlantic and Pacific if the land bridge joining North America and South America were to subside to a depth of 1000 meters along its entire length. Compare the expected distribution with those present today including an explanation of the mechanisms producing both today's and the future distributions. Include chemical, physical, and biological arguments in your discussion. (Cooke)

16. Consider the NH_4^+/NH_3 system in pH - 8.0 seawater. If K', the acid dissociation constant based on concentrations for NH_4^+, were $10^{-9.3}$ what would the ratio of NH_4^+ to NH_3 be? (Hulbert)

17. (a) The atmospheric residence time of particulate NO_3^-, as calculated by our nitrogen cycle, is only 1.2 days. This is rather short. Suggest what incorrect assumptions may have been made or what portions of the budget may be in error (and in what way) to give such a result, i.e. why do you think the cycle gave us such a short, and probably inaccurate, residence time?
(b) A similar situation occurs for $SO_4^=$ in the sulfur cycle, where the calculated atmospheric residence time is ~2.5 days, somewhat short. Analyze this short $SO_4^=$ residence in the way you did NO_3^-. (Duce)

18. A microbiologist claims to have isolated an organism which converts NH_4^+ to NO_3^- using $SO_4^=$ in the absence of air. Calculate the free energy for this reaction at pH = 7. Could such an organism actually exist? If so, what special conditions would favor its growth? (Butler)

19. At the mouth of a small deep estuary a local development company built a housing development and bridge cutting off nearly all exchange with the ocean. The bottom water in the estuary went anoxic. Assume there was no exchange with the surface and bottom, i.e., the deep water was in a closed system. Also assume all the organic matter is mineralized, then what was the final concentration of dissolved oxygen, phosphate, nitrate, ammonia, hydrogen sulfide, and sulfate in the water after enough time elapsed for oxidation of 90% of the organic matter? (Loder)

Starting conditions: S $^{o}/_{oo}$ = 18.07; T = 16C; NO_3 = 4 μMoles/l; NH_4 = 2 μMoles/l; PO_4 = 1 μMole/l; Organic matter = 20 mg/l (Assume average chemical composition for organic matter); O_2 = 100% saturation.

20. Below are data for a silicate section for the Pacific. (a) Calculate the difference between the vertical mass transfers of dissolved silica at 50°N and 30°N. (Hint: You may wish to use the following equation: $J = K_e \frac{dC}{dz} + wC$, where K_e is the diffusion coefficient with an assumed constant value of 10 cm^2/sec and w is the rate of upwelling which is assumed constant with a value of 5 m/yr. Make your own assumption about the value(s) of C.) Be sure to watch your units; the final answer will be a flux having dimensions of $ML^{-2}T^{-1}$. (b) Of this calculated flux, what fraction is used in biological uptake? (Duedall)

Lat 30°N, 155 W		Lat 50°N, 155 W	
Depth (m)	Conc. (μM Si/l)	Depth (m)	Conc. (μM Si/l)
0	<10	0	18
100	<10	100	37
200	<10	200	81
300	13	300	93
400	22	400	111
500	41	500	120
600	62	600	125

E. *Organic Matter in Seawater*

1. You are attending a public hearing of the Durham, New Hampshire Town Council as an expert on marine sciences. The meeting is a real mixed bag of oil executives, environmental scientists, "eco-freaks," "little-old-ladies" and petty government officials. In a discussion of oil spills and biological food chains, someone has asked why is organic chemical oceanography important. Based upon more than just oil, give a two to three sentence answer for the audience at this public hearing. Alternate Problem: Explain why organic chemical oceanography is not important. (Sharp)

2. Summarize (in 50 words or less) the current problems in understanding the sources and sinks of dissolved organic carbon. (Kroopnick)

3. In marine particulate organic matter the carbon to nitrogen ratio varies from about 5:1 near the surface to about 2:1 in deep water. On what basis is the surface-water ratio expected and how would you rationalize the deep-water ratio? (Hulbert)

4. You've just taken a job with Wanta Date, Inc., who have just received a $100K grant to determine the age of organic matter in the deep ocean. It is your job to set up the experimental procedure necessary to collect and analyze (using carbon-14 dating) the age of both dissolved and particulate organic matter from 5 depths in the deep ocean ranging from 1000 m to 5000 m at 2 different locations. The grant includes 20 days of ship time at $2500/day. By using liquid scintillation counting you will need only about 0.5 g of carbon to get a date.

   Please list and discuss: (a) the amounts and sources of organic matter in the deep sea (b) sources of contamination or other factors that will affect your final results (bomb carbon has been found to about 1200 m) (c) methods of sample collection, time necessary to do the experiment (d) is $100K enough? (e) meaning of the results. (Note: a date on dissolved organic matter from the deep Pacific was greater than 3000 years B.P.) (Loder)

5. Draw the distribution of organic carbon (particulate) reported by Menzel and Goering. (a) What inference can you make with regard to the chemical stability of the organic detritus? (b) Is there anything about the way Menzel and Goering present their data that might obscure certain features? Explain. (c) How did the oxidizable carbon in the deep ocean compare with that for surface waters? (Give relative numbers to indicate how refractory the particulates are.) (Duedall)

6. What did Menzel and Goering state concerning the distribution (actual concentrations and vertical profile) of particulate organic carbon below 200 m in the oceans? Give the units and state the reason(s) which they postulated for this type of distribution. (Adams)

7. What effect would sorbed films of organic material (surfactants) have upon the kinetics of calcium carbonate dissolution? Upon precipitation? What effect would this film have upon the equilibrium condition? What effect would organic material have in temporal terms if it simply wet the calcium carbonate but was not sorbed? (Cooke)

8. Humic acids, or those natural organic acids produced by the degradation of vegetable matter in soils, might be expected to undergo reactions of different types and to greater or less extent as they are carried out to sea by rivers and streams and to greater depths by mixing. Explain the effects. (Cooke)

9. Draw as accurately as possible the seasonal distribution of organic aggregates and total phytoplankton in Long Island Sound. (a) Discuss the ecological significance of these distributions. (b) Give at least three reasons why you might expect a high yield of organic aggregates in Long Island Sound. (c) Draw a percentage size-frequency distribution of newly formed aggregates and bacteria-containing aggregates. Give the dimensions (in microns) of the particles. What ecological interpretation can you draw from this diagram? (d) Draw some kind of flow diagram which illustrates the general ecological implications of Riley's theory on organic aggregates. Be sure to include whatever reversible reactions you feel are appropriate. What is the relevance of such a diagram to community structure? (Duedall)

10. Draw a latitudinal plot of aggregates (volume) and phytoplankton for the area from the Sargasso Sea to the North Equatorial current. Give a rough estimate of size of the particles in your figure. (a) What oceanographic feature appears to correlate with particulate distribution near the eastern North Equatorial Current? (b) How does the size of the organic aggregates found on this transect compare with the size of organic aggregates found in Long Island Sound? How can this be explained? (c) What is the fraction (%) of adsorbable organic matter which is present in the total dissolved organic matter? Would you consider this fraction to be depth dependent? Why? (Duedall)

F. *Productivity*

1. (a) What single pigment is essential for all higher plant (except bacteria) photosynthesis systems? (b) Why are other pigments also found in marine phytoplankton? (Include mention of a couple of the other pigments in your answer). (c) How can one measure phytoplankton pigments (or pigment) in the sea? (d) Why is a discussion of deep sea distribution of plant pigments rather boring? (Include how deep, deep sea means in this context). (Sharp)

2. Diagram and describe the timing of a bloom cycle and point out, with examples, what factors cause geographical and temporal variations. (Baier)

3. Plot the relative variation of the listed parameters in seawater through one diurnal cycle during the summer.: O_2^a, pH, phosphate, surface photosynthetic activity, compensation depth. (Mathewson)

4. Explain what effect the photosynthetic activity of phytoplankton in the sea has upon each of the following. Explain each effect briefly. (a) dissolved oxygen concentration (b) the isotopic composition of the dissolved oxygen (c) salinity (d) nitrate concentration (e) ammonia concentration (f) solubility of calcium carbonate (g) iron concentration (h) silicate concentration (i) dissolved organic carbon concentration (j) preformed phosphate (Gordon)

5. What is the effect of photosynthesis upon the following properties of an isolated volume of seawater? Defend each conclusion briefly. (a) dissolved oxygen concentration (b) total inorganic carbon dioxide concentration (TCO_2) (c) carbonate ion concentration (d) total carbon (inorganic + organic) concentration (Gordon)

6. Discuss advantages and disadvantages for marine organisms (plants and animals) being small. (Baier)

7. According to Redfield and other investigators the composition of open water plankton has a fairly constant proportion of N:P of 16:1 (by atoms). However, this ratio was measured in the plankton of the English Channel and was found to vary from 10.5:1 in the winter to 19:1 in the summer. If this is supposedly constant, why would you find the deviation in normal plankton growing in coastal waters (English Channel)? (Adams)

8. Along the California coast, the prevailing winds are from the north in the summer and from the south in the winter. In which season do you expect better fishing? Explain the reasons for your choice (a diagram may be helpful). (Hammond)

9. Man probably, in his most machinistic maliciousness, will not remove the seas from the face of the earth. Assume that he could though, as a totally successful modern Noah, gather million by billion every single living organism from the earth and her seas, but then kill them. As divine planner after this holocaust, you may cart off all the former organisms to an other-worldly burial place or you may leave all the carcasses in the sea. Do you think that life could evolve again in this sea? Briefly justify your answer. Note: You may briefly discourse into life and death, but don't get hung up on the subject, just a statement of definition will do. (Sharp)

10. You have measured the chlorophyll content of an oceanic water sample as 1.257 $\mu g\ l^{-1}$ and the phytoplankton primary productivity as 15.48 $\mu g\ C\ l^{-1}\ day^{-1}$. You may assume a living carbon to chlorophyll ratio of 50:1 and that classical atomic ratios for C:N:P hold both for the phytoplankton and the nutrients within the water. What should be the concentration of orthophosphate in the water? How long would it take for the phytoplankton to exhaust the supply of phosphate? You have just discovered data that shows the nitrate content of this water sample as 0.09 μg-atN/l and the nitrite content as 0.02 μg-atN/l. What does this tell you about the total available nitrogen? (Sharp)

G. *Geochemical Cycling*

1. *Silicate and clay equilibrium*

1. The most complex parts of the aquatic ecosystem are its interfaces with air, land, and sediments. Chemically, these interfaces may be quite different but there are a number of common principles which apply to all. Discuss in particular the accumulation of charge at the boundary between phases for a particle of silica which begins on a desert, is blown by the wind into a rainy upland where it comes down with the rain to a lake, runs via a river to the sea and eventually settles to the sea floor. What different effects would be induced by its surface charge at each stage of the journey? Note especially any effects of air or water pollution. (Butler)

2. Orthosilicic acid is approximately 10% dissociated in the oceans according to the following equation: $Si(OH)_4 = H^+ + SiO(OH)_3^-$ That is, about 10% occurs in the ionic, silicate, form, and 90% in the undissociated acid form. Calculate pK'_1 for orthosilicic acid in seawater of average oceanic composition. (Gordon)

3. How do MacKenzie and Garrels propose to solve the silica bicarbonate balance in the oceans, which are considered to be in "steady state," by their reverse weathering scheme? Name one of the clay phases which would be at equilibrium in their ocean (they listed three). (Adams)

4. Sillen proposes an equilibrium ocean; explain what is meant by equilibrium in his model. (Duedall)

5. (a) What factor(s) might limit the usefulness of the equilibrium theory proposed by Sillen?
   (b) Based on the theory of Sillen, the pH of seawater in the ocean is controlled by some type of clay/seawater interaction, yet when we make artificial seawater containing no clays we find the pH of the solution to be about the same as natural seawater. Explain this and also explain how the Sillen theory can be verified. (Duedall)

6. Why is the composition of seawater relatively constant? Outline the strengths and weaknesses of the thermodynamic, kinetic and geochemical balance models proposed by Sillen, Broecker and Goldschmidt. (Reeburgh)

7. The "equilibrium" approach used to explain why seawater has its particular composition says: solid phases must be in equilibrium with the ocean and atmosphere (assume components of Na_2O, K_2O, CaO, MgO, HCl, H_2SO_4, CO_2, H_2O, SiO_2, Al_2O_3) if we have a univarient system. If this is true, would you expect seawater to change its composition if the temperature changes? (Hammond)

8. In many areas kaolinite is the mineral that precedes the final dissolution of solids by the agents of weathering. In other areas gibbsite is the persistent species. Given the mineral assemblage kaolinite-gibbsite-K mica calculate the equilibrium concentrations of the ions involved. That is, construct a model sediment consisting of 3 mineral phases and ask if it coincides with observed seawater ion concentrations.

The pertinent relations are:

eq. 1: $\log K_1 = 6.5$

$$2\ KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O = \underset{\text{kaolinite}}{3\ H_4Al_2Si_2O_9} + 2K^+$$

K mica

eq. 2: $\log K_2 = -7.6$

$$2\ KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 18\ H_2O = \underset{\text{gibbsite}}{3\ Al_2O_3 \cdot 3H_2O} + 2K^+ + \underset{\text{dissolved silica}}{6H_4SiO_4}$$

K mica

eq. 3: $\log K_3 = -4.7$

$$H_4Al_2Si_2O_9 + 5H_2O = Al_2O_3 \cdot 3H_2O + 2H_4SiO_4$$

(a) Construct a plot showing the fields of stability for each of the above 3 phases. Hint: Plot log (K^+/H^+) versus log H_4SiO_4 then mark off the areas occupied by each phase. Each equation (1,2,3) represents a line separating two of the phases in such a diagram. (b) Why do we plot log (K^+/H^+)? (c) Indicate where seawater would plot on the diagram. (d) Are the concentrations of H^+, K^+, and silica fixed by their system? (e) Is this sytem compatible with Sillen's thesis that the chemical composition of seawater is controlled by ion exchange with the sediments? (Kroopnick)

2. *Geochemical problems and sediments*

1. How thick would the ocean be on a 12" globe? (Reeburgh)

2. 30 million cubic kilometers of ice exist today: If distributed uniformly over the earth, how thick a layer would it form? (Reeburgh)

3. Assume the earth accreted from solid particles. (a) What evidence is there the earth has ever melted (2 reasons)? (b) What are possible sources of the energy (give 2) needed to do this? (Hammond)

4. Assume: (a) that in passing from a glacial maximum to a glacial minimum in the Pleistocene 4×10^7 km^3 of ice is melted in 20,000 years, (b) that the melting takes place at a uniform rate throughout the period, (c) that 1 m^3 of ice weighs 900 kg. What is the fraction of the total insolation required to cause this melting? (Duce)

5. (a) The method of geochemical balances involves one or more assumptions and types of input data. What are these? Which are the most reliable of the input data and which the least reliable? (b) Give an example of an element which balances and one which does not. (c) What is the significance of the geochemical balance to the history of the oceans? (Gordon)

6. Considering the mass balance between rivers and oceans, why has the ocean not been filled in by all those sediments? (Sharp)

7. Write a simple materials balance equation for the formation of the ocean and sediments by the weathering of primary igneous rocks. Identify each term in the equation. (Duedall)

8. By his actions as an erosional agent, man has selectively increased the weathering rates of certain types of sedimentary and hydrothermal deposits (such as ore bodies, coal fields, etc.). Assume that chemical oceanographers can detect 1% changes in seawater chemistry, and that natural "sinks" are unaffected by man. Calculate the number of years required (at present rates) for man to make a detectable change in seawater chemistry for each of the following: (Hammond)

		seawater conc. g/kg	Res. time	man's input (10^9 tons)	Source
Rock salt	(as NaCl)	30	2.6×10^8 y	2	B. Mines, 1973
Sulfur	(as SO_2)	2.71	1.1×10^7 y	2.4	SRI, 1968
Carbon	(as CO_2)	0.105	1×10^5 y	1800	SCEP, 1967
Phosphorus	(as PO_4)	0.090×10^{-3}	?	0.6	SCEP, 1966
Lead	(as Pb)	1.0×10^{-7}	2×10^3 y	0.035	Patterson, 1966

Mass of Ocean = 1.4×10^{24} g

9. Recently an attempt to determine the relative trade wind speeds over a period of some 700,000 years has been reported. The technique used was to determine the size distribution of quartz grains as a function of depth in the sediment in material from deep water off the Saharon coast. How could this be done and what are the key assumptions? (Hulbert)

10. (a) What is a nepheloid layer? (b) Give one postulate for the occurrence of a nepheloid layer. (c) Compare the mean concentrations of suspended matter for the Atlantic versus the Pacific Ocean. (Give in units of mg/200 liters.) (d) Draw a set of curves which contrast the bottom profile and the thickness of the nepheloid layer. What possible interpretation can be drawn from this figure? (Duedall)

11. In the paper by Ewing and Thorndike (Science 147:1291-1294 (1965)), the authors calculate that the effect of suspended matter of concentration 0.50 g/200 l on the density of seawater approaches that of a change in temperature of 0.01C. Verify this calculation. Assume a salinity of 35 ppt and a density of 2.2 g/cm^3 for the clay particles. If need be consider the temperature of the ocean at the point of sampling as 5C. A check on your answer can be obtained by determining the change in density of seawater if its temperature changed by 0.01C. (Duedall)

12. Nepheloid Layer: (a) Describe what is meant by a nepheloid layer. (b) A nepheloid layer was discovered off the continental slope of the mid-Atlantic bight. What possible assumptions can you make with regard to the origin of the nepheloid layer. Which assumption do you favor and why? (Duedall)

13. What kind of relationship would you expect to exist between suspended matter and salinity in surface waters near river-estuary systems? What is the significance of such relationships? (Duedall)

14. During the past few years several workers at UNH have reported large numbers of microscopic pellets (hereafter referred to as MPX-1, Mystery pellets, X-1) occurring in our coastal waters of the Gulf of Maine and some offshore banks. We know the following about them: (a) They occur during the spring time. (b) Size is about 4μ diameter egg shaped. (c) Their number ranges from 10^6 to 10^8 per liter and they show up as a peak on culture counter data on size distribution of particles in seawater. (d) They appear to crumble or dissolve if put in distilled water. (e) They can be examined by collection onto filters or settling in an inverted microscope. (f) They do not appear to be individual live organisms. (g) Their composition is unknown although others have reported similar particles high in barium sulfate. A "publish or perish professor" has just assigned these pellets to you as a Master's thesis. Set up and describe the experiments and methods you would use to determine size, number, composition and origin of these particles. Make sure you include such things as how much water needs to be collected to get enough for chemical analysis, how to concentrate and analyze them, etc. (Loder)

15. Knowing all there is to know about the electrochemistry of the sea, you are confronted by the EPA for an environmental baseline statement about two small salt ponds in Southern California. Walt Disney Enterprises, in manufacturing 100,000 plastic trees, has accumulated some waste products that they wish to dump into one or both of the salt ponds. The EPA wants your advice.

One of the salt ponds has a salinity of 11.7 °/oo and the other has a salinity of 105 °/oo. The little information available suggests that the ponds are of recent ocean origin and that the salinity differences are due to one having been subjected to extensive evaporation while the second had received considerable fresh water input (ion-free rain water). From lecture notes you should realize that seawater of 35 °/oo salinity (closest reference chlorinity is 19 °/oo) has a predictable pH of 8.12; you may assume that the salt ponds and seawater resemble pure NaCl solutions in calculations of ionic strength and molality.

The Disney waste is a complicated iron-clay slurry for which you have been given the formula $(FeAl_6Si_6O_{20}(OH)_4)$ and you know that at a pH above 8.0 this clay will react in a manner in which sulfate is reduced to pyrite (FeS_2) which precipitates; the resultant clay ($Al_2Si_2O_5(OH)_4$) will also precipitate. The reaction is as follows:

$$95.5\ FeAl_6Si_6O_{20}(OH)_4 + 191\ SO_4^{=} + 47.8\ CO_2 + 55.7\ C_6H_{12}O_6 + 238.8\ H_2O \longrightarrow$$
$$286.5\ Al_2Si_2O_5(OH)_4 + 95.5\ FeS_2 + 382\ HCO_3^-$$

You fear that at a lower pH, this clay will form a powdery floc and float on the surface completely smothering the pond.

Would you suggest to the EPA either (which one), neither, or both ponds for the Disney dumping? Do you think alumino-silicates could alter salinity, pH, major ions, minor ions? (Sharp)

16. If the equilibrium constant for the reaction $Na^+(aq)$ + K-montmorillonite $\rightleftharpoons K^+(aq)$ + Na-montmorillonite is 2.0 ($K_{eq} = 2.0$), what is the equilibrium ratio of X_{Na^+}/X_{K^+} on the surface of montmorillonite equilibrated with (a) average river water (b) seawater? If the exchange were relatively slow, what can you conclude about the change in chemistry that would occur in the interstitial water of montmorillonite-rich sediments that are rapidly deposited by a river in a marine environment? Assume symmetrical regular solution on a clay surface with A = 1, B = 0 and all exchange sites occupied by Na^+ and K^+.

River: $a_{Na^+} = 2.6 \times 10^{-4}$ $a_{K^+} = 0.56 \times 10^{-4}$ Seawater: $a_{Na^+} = 3.56 \times 10^{-1}$ $a_{K^+} = 6.3 \times 10^{-3}$

(Morse)

17. The concentration of H_4SiO_4 in surface seawater is 10^{-6} M. How long should it take to dissolve a spherical quartz sand grain of 0.2 mm diameter if diffusion is the rate controlling mechanism? D = 10^{-5} cm^2/sec, ignore solubility change with size. (Morse)

18. The predominant carbonate sediments found under the sea are calcite and aragonite but thermodynamically one would predict magnesite and dolomite. Considering both hydrogenous and biogenous sediments, explain why thermodynamics has led us astray in our predictions. (Sharp)

19. If the sulfur ion concentration in reducing sediments (EH = -0.3) were controlled by the formation of Pyrrhotite (FeS), calculate the expected concentration of $SO_4^{=}(aq)$ within the sediment. All the information you need is given below. (Kroopnick)

Use pH = 8.1, EH = -0.3, $Fe^{+2}_{aq} = 10^{-7}M$ $\frac{RT}{2.303F} = 0.06$ for T = 25C; $\frac{.06}{8} = 0.0075$

Useful Information (State clearly any further assumptions)

$\Delta F = nFE = -RT\ln K$

$E = E^0 + \frac{RT}{nF} \ln Q$

$HS^- + Fe^{+2} = H^+ + FeS$	log K = 4.4
$H^+ + HS^- = H_2S$	log K = 7
$H^+ + S^{=} = HS^-$	log K = 14
$HSO_4^- = H^+ + SO_4^{=}$	log K = -1.9
$H_2S + 4H_2O = SO_4^{=} + 10H^+ + 8e^-$	$E^0 = 0.30$
$H_2S + 4H_2O = HSO_4^- + 9H^+ + 8e^-$	$E^0 = 0.29$
$HS^- + 4H_2O = SO_4^{=} + 9H^+ + 8e^-$	$E^0 = 0.25$

20. Will Sr^{+2} form a solid solution with $BaSO_4$ and if so, calculate the Ba/Sr ratio expected in marine sediments. (Kroopnick)

log K_{SrSO_4} = -6.55 (5C)	log $[Ba^{+2}]$ = -6.34
	log $[Sr^{+2}]$ = -4.04
log K_{BaSO_4} = 10.2 (5C)	log $[SO_4^{=}]$ = -1.55

21. What correlation exists between topography and the distribution of calcareous sediments? Explain why. (Hammond)

22. Give the mode of origin of each of the following minerals found in deep sea: (a) Kaolinite ($Al_2Si_2O_5(OH)_4$) (b) Barite ($BaSO_4$) (c) Quartz (SiO_2) (Kroopnick)

23. Sediment thickness near the margins of the Atlantic is about 2 km. The "age" of the Atlantic is about 200 my. What is the average deposition rate? What should the sediment thickness be halfway from New York to the Mid Atlantic Ridge? (Hammond)

24. The excess Th^{230} at the top of a sediment core is 30 dpm/g and at the depth of 50 cm, 7.5 dpm/g. Calculate the average sedimentation rate for this core. State the assumptions you use in the calculation (the decay constant of Th^{230} is 9.22×10^{-6} yr^{-1}). (Ku)

H. Models

1. What is the usefulness of a chemical model for seawater? Describe very briefly two chemical models for seawater. (Gordon)

2. In the international oceanographic community today, we are being inundated with biological models, many of which are horrible. What value are models of this nature and what precautions should one take before embarking on such a grandiose scheme? (Sharp)

3. Assume that the oceans may be modeled as a dilute aqueous solution in a box with vertical walls. How much water would need to be removed to lower sea level by 100 meters? How does this quantity compare with the total volume of the oceans? What period of time would be required to supply this much water to the continents at the current rate of 3×10^4 km^3/year? Comment upon the assumed shape of the ocean basins. What error, if any, will be divergence between this model and the actual shape cause in the calculated quantity of water needed to cause a 100 m change of sea level? (Hulbert)

4. Explain the following observations: Estimation of the mean residence times of water molecules in the deep ocean from the natural radiocarbon using a simple two-box model (surface ocean and deep ocean separated by main thermocline) gives values that tend to be lower limits. (Ku)

5. Assume the ocean is a 2-layered box with the following properties:

	Surface Ocean	Deep Ocean
Depth	100 M	4000 M
ΣCO_2 (mmol/l)	2.00	2.30
Alk (meq/l)	2.18	2.40
PO_4	0	2.5 μmol/l
NO_3^-	0	36 μmol/l

Upwelling rate = 4 M/yr. Calculate the particulate flux of carbon from the surface ocean to the deep ocean. What fraction of this is as tissue and what fraction is shell material (Hint: remember that the only way to change alkalinity is by solution or precipitation of $CaCO_3$ and that each $CO_3^=$ ion carries 2 charges.)? (Hammond)

6. Assume the ocean is a 2-layered box. The upper box is 100 m deep, the lower box 4000 m deep. The 2 boxes exchange water at a rate of w (units are cubic meters/square meter per year = m/yr.) (a) Plot schematically $PO_4^=$ versus depth, ΣCO_2 versus depth, O_2 versus depth. (b) Briefly explain the reasons for the shape of the curves. (c) Assume $PO_4^=$ is the limiting nutrient in plant growth. What 2 factors control the rate at which carbon is fixed into plant tissue. Can you express this mathematically? (d) What geochemical tool(s) is useful in determining w? As a taxpayer, how much public money would you be willing to spend to measure w? (Hammond)

7. Assume that ocean circulation can be adequately treated by the one-dimensional box model. Then the rate of upwelling is 2 meters per year, and mean ocean depth is 4000 meters.

Diatoms are microscopic plants which secrete silica tests (i.e. shells) and live in the ocean. In many regions their productivity is limited by the availability of dissolved SiO_2. In the deep Pacific $[SiO_2] = 0.15\ \mu mol/cm^3$. (a) Calculate the flux ($mol/cm^2\ yr$) of particulate silica which falls from the surface ocean. (b) If 1% of this silica is insoluble, what is the residence time of $[SiO_2]$ in the ocean? (c) In glacial times, the ocean may have circulated twice as fast as today. What immediate effect would this have on productivity? (d) If the rate of supply of silica in river water remained constant in part c, what would eventually have to happen to deep ocean SiO_2 if part b remained true? (Hammond)

I. *Isotopes, Radioactive and Stable*

1. (a) Contrast man's natural radiation burden on a ship at sea, along a coast, and high up on the mountains. (b) What are the dominant sources of radiation in each of the above cases and in seawater? (c) If the main source of radiation in the sea were 40K ($t_{\frac{1}{2}}$ = 1.3 x 10^9 years), would the radiation burden of life in the sea have been substantially different about a million years ago? Why? How about in the Cambrian when life was emerging, say about 1300 million years ago? (d) What are the various sources of radionuclides which occur in the oceans? Give two examples of radionuclides from each source. It's an ill wind that blows no good. List a use which has been made of each of the nuclides you listed in the fields of oceanography, biology, or other earth sciences. (e) Radium-226 appears to be more concentrated in deeper than in shallower waters of the Pacific Ocean. How has this been, or might it be, explained? (Gordon)

2. (a) The radionuclide in largest concentration in seawater is _____. (b) Describe and explain the radium profiles in the oceans and in sediments. (c) Thorium-232 has a half-life of 1.4 x 10^{10} years. Thorium-230 derived from U^{238} decay has $t_{\frac{1}{2}}$ = 8 x 10^4 years. Why are these nuclides not found in seawater? (Mathewson)

3. Explain the observation: The U^{238}, U^{234}, Th^{230} and Ra^{226} one finds in a seawater sample has concentrations (in units of dpm/l) of 2.47, 2.84, 0.0004 and 0.35, respectively. (Ku)

4. If no more artificial radioactivity is added to the oceans, how will the level of total radioactivity in the oceans 50 years from now compare with that of today? a billion years from now? Briefly explain your conclusion, stating any assumptions you have to make. (Gordon)

5. Potassium-40 is a naturally occurring radio-isotope in seawater that decays to Argon-40 at an approximate rate of 50 atoms/minute - liter of seawater. How long would it take to make a 1% change in the argon concentration in seawater (assume seawater at 5C and 35 opt)? Would the time required for the 1% increase be significant in terms of residence time of deep ocean water? (Loder)

6. Assuming that radioactive atoms and particles in the atmosphere follow first order kinetics, i.e. $N = N_0 e^{-\lambda t}$, where N_0 = # of radioactive atoms or atmospheric particles present at time zero, N = # of radioactive atoms or atmospheric particles present at time t, λ = the decay or removal constant for radioactive atoms or atmospheric particles.

   Prove that τ, the mean life expectancy of any radioactive atom or any particle in the atmosphere, is equal to $1/\lambda$. Hint: The average life is found from the sum of the times of existence of all the atoms or particles divided by the initial number of atoms or particles present at time equal 0. (Duce)

7. Penguins captured in Antarctica have been dated by C^{14} as being 1000 years old, yet their life span is known to be only a few years. Explain this dilemma. (Hammond)

8. Suppose the Marianna Trench (located in the western equatorial Pacific) was used as a dumping ground for radioactive waste water from nuclear reactors. Would you expect the Sr^{90} from this waste to appear first in the bones of penguins or Japanese sea gulls? Explain. (Hammond)

9. Explain why the vertical distribution of the δC^{13} of dissolved inorganic carbon in the sea shows a minimum at a depth below the photic zone. (Ku)

10. A certain isotopic evaporation process was studied. Analyses of the liquid and vapor in equilibrium with each other were performed. Expressed in terms of the same standard, $\delta_V = -50$ ‰ and $\delta_L = +50$ ‰. Calculate α, the fractionation factor for the process. (Gordon)

J. Pollution of the Sea

1. As a brand new hot-shot environmentally conscious college grad, you've been hired by a small dredging company to prepare an impact statement concerning the chemical effects of dumping 100,000 cu. yds. of anoxic estuarine sediments 5 miles off the coast in 100 feet of water. What do you expect might be the effects of this dredging and dumping operation on the chemistry of the water in the dredge site and dumping area involved? You may mention how the chemical changes might ultimately affect the biology as well. (Loder)

2. Explain some of the chemical characteristics of a desalination plant discharge stream as a pollutant. Consider a plant which utilizes a seawater as its raw material. (Gordon)

3. (a) What considerations must be made in choosing the process for a plant for production of fresh water from seawater? (b) What considerations must be made in choosing the locations for these plants? (c) What chemical problems commonly occur in such plants? (Gordon)

4. Would a sulfuric acid waste from an industrial plant be a dangerous pollutant in the ocean? Give and explain the reasons for your conclusion. (Gordon)

5. If we are forced to rapidly accelerate the rate of gaseous geochemical pollution by steam vents and fumaroles because we need geothermal power and therefore we drill a great number of geothermal steam wells, what might be the marine chemical consequences? Consider the salinity and pH of the oceans mainly. Do not attempt a detailed or quantitative answer. (Gordon)

6. What criteria must be applied to decide whether an industrial waste product will become a dangerous pollutant? (Gordon)

7. Assume that you are a principal investigator with an interest in coastal oceanography. You have a healthy equipment budget and a laboratory full of instruments that are dying of old age. The attached data sheet was sent to you.

   Evaluate the model Brand X Portable Water Quality Monitor in terms of what it does, how well it does it, the environmental ranges you expect to encounter and the other equipment (e.g. large ship, winch, samplers, thermometers) its use might obviate. Would you buy the monitor? Why or why not? What other fields might find this instrument useful? The fact sheets for any of today's monitoring instruments should be attached to this question. (Reeburgh)

8. You have been hired by the Environmental Protection Agency (EPA) to monitor pollution in the Delaware Bay. You discover a waste barge from the von Brücke chemical company dumping its contents into the bay and are able to get a sample of their waste and a sample of the bay water after the event. Of course, your statement that you saw them dumping is insufficient documentation on which to prosecute. Being a clever chemist, you can get some average river water and average ocean water trace metal values and you can run iron, silver, and zinc analyses on the two samples you got. (a) With the listed results and your knowledge of conservative constituents in seawater, what can you give your legal staff?

Water	°/oo S	ppbFe	ppbAg	ppbZn
Seawater	35	3.4	0.1	5
River Water	0	670	0.3	10
Waste	0	1950	170	480
Bay Water	25	211.5	1.86	11.17

(b) How would you run the trace metal analyses for the EPA and what precaution should you take in so doing? (Sharp)

COURSE REFERENCE LISTS

A. *Introduction - General Reference Books*

Andersen, N.R. 1973. (Convener). Chemical Oceanographic Research: Present Status and Future Direction. Office of Naval Research ACR - 190.

Barnes, H. 1959. Apparatus and Methods of Oceanography, Part 1: Chemical. Allen and Unwin.

Berner, R.A. 1971. Principles of Chemical Sedimentology. McGraw-Hill.

Broecker, W.S. 1974. Chemical Oceanography. Harcourt Brace Jovanovich.

Church, T., ed. 1975. Marine Chemistry in the Coastal Environment. ACS Symp. Series V. 18.

Dyrssen, D. and D. Jagner, eds. 1972. The Changing Chemistry of the Oceans. Wiley-Interscience.

Emery, K.O. 1969. A Coastal Pond - Studied by Oceanographic Methods. Elsevier.

Gibb, T.R.P., Jr., ed. 1975. Analytical Methods in Oceanography. ACS Advances in Chemistry Series No. 147.

Goldberg, E.D. 1972. A Guide to Marine Pollution. Gordon and Breach.

Goldberg, E.D., ed. 1974. The Sea, V 5: Marine Chemistry. Wiley-Interscience.

Goldberg, E.D., ed. 1975. The Nature of Seawater. Berlin. Dahlem Konferenzen.

Gould, R.F., ed. 1967. Equilibrium Concepts in Natural Water Systems. ACS Advances in Chemistry Series, No. 67.

Harvey, H.W. 1955. The Chemistry and Fertility of Sea Water. University Press, Cambridge, England.

Hem, J.D., ed. 1970. Nonequilibrium Systems in Natural Water Chemistry. ACS Advances in Chemistry Series, No. 106.

Hill, M.N., ed. 1963. The Sea, V. 2: Ideas and Observations, The Composition of Sea Water, Comparative and Descriptive Oceanography. Wiley-Interscience.

Hood, D.W., ed. 1971. Impingement of Man on the Oceans. Wiley-Interscience.

Horne, R.A. 1969. Marine Chemistry. Wiley-Interscience.

Martin, D.F. 1968. Marine Chemistry, V I and II. Marcel Dekker, New York.

Marx, F. 1967. The Frail Ocean. Ballantine.

Mero, J.L. 1965. The Mineral Resources of the Sea. Elsevier.

National Academy of Sciences. 1971. Marine Chemistry: A report of the Marine Chemistry Panel of the Committee on Oceanography. Washington, D.C.

Raymont, J. 1963. Plankton and Productivity in the Oceans. Pergamon.

Riley, J.P. and R.G. Chester. 1971. Marine Chemistry. Academic.

Riley, J.P. and G. Skirrow, eds. 1965 and 1975. Chemical Oceanography 1st ed. Vol. 1 and 2, 1965; 2nd ed., Vol. 1 to 6, 1975. Academic.

Scientific American. 1971. Oceanography.

Sears, M., ed. 1961. Oceanography. AAAS Pub. No. 67, Washington, D.C.

Strickland, J.D.H. and T.R. Parsons. 1968. A Practical Handbook of Seawater Analysis. Bull. 167. Fish. Res. Bd. Can.

Stumm, W. and J.J. Morgan. 1970. Aquatic Chemistry. Wiley-Interscience.

Sverdrup, H.U., M.W. Johnson and R.H. Fleming. 1942. The Oceans: Their Physics, Chemistry, and General Biology. Prentice-Hall.

B. *Physical and Thermodynamic Properties of Water and Sea Water*

Berner, R.A. 1971. Physical chemistry of carbonates in the oceans. In: W. Hey (ed.), Studies in Paleo-Oceanography. SEPM Spec. Pub. No. 20.

Butler, J.N. 1964. Ionic Equilibrium. Addison-Wesley.

Connors, D.N. and K. Park. 1967. The partial equivalent conductances of electrolytes in seawater: a revision. Deep-Sea Res. 14: 481-484.

Culberson, C.H. and R.M. Pytkowicz. 1973. Ionization of water in sea water. Mar. Chem. 1: 309-316.

Disteche, A. 1974. The effect of pressure on dissociation constants and its temperature dependency. p. 81-122. In: E.D. Goldberg (ed), The Sea, v. 5. Wiley-Interscience.

Dyrssen, D. and M. Wedborg. 1974. Equilibrium calculations of the speciation of elements in seawater. p. 182-196. In: E.D. Goldberg (ed), The Sea, v. 5. Wiley-Interscience.

Duedall, I.W. and P.K. Weyl. 1967. The partial equivalent volumes of salts in sea water. Limnol. Oceanogr. 12: 52-59.

Garrels, R.M. and M.E. Thompson. 1962. A chemical model for seawater at 25°C and one atmosphere total pressure. Amer. J. Sci. 260: 57-66.

Horne, R.A. 1969. Marine Chemistry. Wiley-Interscience.

Horne, R.A. (ed). 1972. Water and Aqueous Solutions. Wiley-Interscience.

Hunt, C.A. and R.M. Garrels. 1973. Water. W. W. Norton, New York.

Latimer, W.M. 1952. Oxidation Potentials. Prentice Hall.

Leyendekkers, J.V. 1976. Thermodynamics of Seawater, Part 1. Marcel Dekker, New York.

Mehrbach, C., C.H. Culberson, J.E. Hawley, and R.M. Pytkowicz. 1973. Measurements of the apparent dissociation constants of carbonic acid in sea water at atmospheric pressure. Limnol. Oceanogr. 18: 897-907.

Millero, F.J. 1974. Seawater as a multicomponent electrolyte solution. p. 3-80. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

National Academy of Sciences. 1959. Conference on Physical and Chemical Properties of Sea Water, Pub. 600.

Park, K. 1964. Partial equivalent conductance of electrolytes in sea water. Deep-Sea Res. 11: 729-736.

Pytkowicz, R.M. and D.R. Kester. 1971. The physical chemistry of sea water. In: H. Barnes (ed.), Oceanogr. Mar. Biol. Ann. Rev. 9: 11-60.

Sillen, L.G. 1961. The physical chemistry of sea water. In: M. Sears (ed.), Oceanography. AAAS Publ. No. 67, pp. 549-581.

Sillen, L.G., and A.E. Martell. 1971. Stability Constants. ACS Spec. Publ No. 25.

Stumm, W. and P.A. Brauner. 1975. Chemical speciation. p. 173-239. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 1. Academic.

Thompson, T.G. and H. Wirth. 1932. Specific gravity of sea water at 0C in relation to the chlorinity. J. Conseil. 6: 232-240.

Whitfield, M. 1975. Sea water as an electroyte solution. p. 44-171. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 1. Academic.

Whitfield, M. 1975. The electroanalytical chemistry of sea water. p. 1-154. In: Riley, J.P. and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 4. Academic.

C. *Composition and General Nature of Sea Water*

1. *Salinity - Definitions, measurements and variations*

Carritt, D.E. and J.H. Carpenter. 1959. The composition of sea water and the salinity-chlorinity-density problems. NAS-NRC publ. 600, p. 67-86.

Chave, K.E. 1971. Chemical reactions and the composition of sea water. J. Chem. Education. 48: 148-151.

Cox, R.A., F. Culkin, R. Greenhalgh, and J.P. Riley. 1962. The chlorinity, conductivity, and density of sea water. Nature 193: 518-520.

Cox, R.A., F. Culkin, and J.P. Riley. 1967. The electrical conductivity/chlorinity relationship in natural sea water. Deep-Sea Res. 14: 203-220.

Johnston, R. 1964. Recent advances in the estimation of salinity. Oceanogr. Mar. Biol. Ann. Rev. 2: 97-120.

Knudsen, M. 1901. Hydrographical Tables, Copenhagen, 66 pp.

Lyman, J., R.F. Barquist and A.V. Wolf. 1958. A new method for direct salinity determination. J. Mar. Res. 17: 334.

Morris, A.W. and J.P. Riley. 1964. The direct gravimetric determination of the salinity of sea water. Deep-Sea Res. 11: 899-904.

Morris, A.W. and J.P. Riley. 1966. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. Deep-Sea Res. 13: 699-705.

Wallace, W.J. 1974. The Development of the Chlorinity-Salinity Concept in Oceanography. Elsevier, Amsterdam.

Wilson, T.R.S. 1975. Salinity and the major elements of sea water. p. 365-413. In: J.P. Riley, and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 1. Academic.

Wooster, W.S., A.J. Lee and G. Dietrich. 1969. Redefinition of salinity. Limnol. Oceanogr. 14: 437-438.

2. *Major and minor ions in sea water*

Brewer, P.G. 1975. Minor elements in sea water. p. 415-496. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 1. Academic.

Broecker, W.S. 1971. The kinetic model for the chemical composition of sea water. Quarternary Res. 1: 188-207.

Culkin, F. and R.A. Cox. 1966. Sodium, potassium, magnesium, calcium and strontium in sea water. Deep-Sea Res. 13: 789-804.

Kester, D.R., I.W. Duedall, D.N. Connors and R.M. Pytkowicz. 1967. Preparation of artifical sea water. Limnol. Oceanogr. 12: 176-79.

Kester, D.R. and R.M. Pytkowicz. 1968. Magnesium sulfate association at 25°C in synthetic sea water. Limnol. Oceanogr. 13: 670-674.

Kester, D.R. and R.M. Pytkowicz. 1969. Sodium, magnesium, and calcium sulfate ion-pairs in seawater at 25°C. Limnol. Oceanogr. 14: 686-692.

Kester, D.R. and R.M. Pytkowicz. 1970. Effect of temperature and pressure on sulfate ion association in sea water. Geochim. Cosmochim. Acta. 34: 1039.

Lyman, J. and R.F. Fleming. 1940. Composition of sea water. J. Mar. Res. 3: 134-146.

3. *Origin of seawater*

Arrhenius, G., B.R. De and H. Alfvén. 1974. Origin of the ocean. pp 839-862. In: E.D. Goldberg (ed.), The Sea, v. 5. Wiley-Interscience.

Conway, E.J. 1942. Mean geochemical data in relation to oceanic evolution. Proc. Roy. Irish Acad. B48: 119-159.

Conway, E.J. 1943. The chemical evolution of the ocean. Proc. Roy. Irish Acad. B48: 161-212.

Gibbs, R.J. 1970. Mechanisms controlling world water chemistry. Science 170: 1088-1090.

Holland, H.D. 1965. The history of ocean water and its effect on the chemistry of the atmosphere. Nat. Acad. Sci. Symposium. 53: 1173-1183.

MacIntyre, F.T. 1970. Why the sea is salt. Sci. Amer. 223: 104-115.

Mackenzie, F.T. and R.M. Garrels. 1966. Chemical mass balance between rivers and oceans. Amer. J. Sci. 264: 507-525.

Mackenzie, F.T. 1975. Sedimentary cycling and the evolution of sea water. p. 309-364. In: J.P. Riley and G. Skirrow (eds.), Chemical Chemical Oceanography, 2nd ed., v. 1. Academic.

Rubey, W.W. 1955. Development of the hydrosphere and atmosphere with special reference to the probably composition of the early atmosphere. Geol. Soc. Amer. Spec. Pap. 62: 631-650.

Rubey, W.W. 1961. Geologic history of sea water: An attempt to state the problem. G.S.A. Bull. 62: 1111-1147.

Sillen, L.G. 1963. How has sea water got its present composition? Svensk Kemisk Tidskrift 75: 161-177.

Sillen, L.G. 1967. The ocean as a chemical system. Science 156: 1189-1197.

D. *Physical Processes of the Ocean*

Blanchard, D.C. 1963. The electrification of the atmosphere by particles from bubbles in the sea. Progress in Oceanography 1: 73.

Bowden, K.F. 1975. Oceanic and estuarine mixing processes. p. 1-41. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed. v.1. Academic.

Junge, C.E. 1972. Our knowledge of the physico-chemistry of aerosols in the undisturbed marine environment. J. Geophys. Res. 77: 5183.

Knelman, F., N. Dombrowski, and D.M. Newitt. 1954. Mechanism of bursting bubbles. Nature 173: 261.

Lemich, R. 1972. Adsubble processes: Foam fractionation and bubble fractionation. J. Geophys. Res. 77: 5204.

MacIntyre, F. 1968. Bubbles: A boundary-layer "microtome" for micron-thick samples of a liquid surface. J. Phys. Chem. 72: 589.

MacIntyre, F. 1972. Flow patterns in breaking bubbles. J. Geophys. Res. 77: 5211.

MacIntyre, F. 1974. Chemical fractionation and sea surface microlayer processes. pp. 245-300. In: E.D. Goldberg (ed.), The Sea, v. 5. Wiley-Interscience.

Medwin, H. 1970. In situ acoustic measurements of bubble population in coastal ocean waters. J. Geophys. Res. 75: 599.

Monahan, E.C. 1968. Sea spray as a function of low elevation wind speed. J. Geophys. Res. 73: 1127.

Monahan, E.C. 1971. Oceanic whitecaps. J. Phys. Oceanogr. 1: 139.

Moore, D.J. and B.J. Mason. 1954. The concentration, size distribution, and production rate of large salt nuclei over the oceans. Quart. J. Roy. Met. Soc. 80: 583.

Wallace, G.T. Jr., G.I. Loeb, and D.F. Wilson. 1972. On the flotation of particulates in sea water by rising bubbles. J. Geophys. Res. 77: 5293.

Woodcock, A.H. 1972. Smaller salt particles in oceanic air and bubble behavior in the sea. J. Geophys. Res. 77: 5316.

E. *Dissolved Gases in Sea Water*

1. *Non-carbon dioxide*

a. *Distribution and solubility*

Battino, R. and H.L. Clever. 1966. The solubility of gases in liquids. Chem. Rev. 66: 396-463.

Benson, B.B. 1965. Some thoughts on dissolved gasses in the oceans. p. 91-108. In: Symposium on Marine Geochemistry. Univ. Rhode Island occ. publ. no. 3.

Benson, B.B. and P.D.M. Parker. 1961. Relations among the solubilities of nitrogen, argon and oxygen in distilled water and sea water. J. Phys. Chem. 65: 1489-1496.

Bieri, R.H. 1974. Dissolved conservative gases in seawater. p. 199-218. In: E.D. Goldberg, (ed.), The Sea, v. 5. Wiley-Interscience.

Broecker, W.S. and T.H. Peng. 1971. The vertical distribution of radon in the BOMEX area. Earth Planet. Sci. Lett. 11: 99-108.

Broecker, W.S. 1970. Man's oxygen reserves. Science 168: 1537-8.

Carpenter, J.H. 1966. New measurements of oxygen solubility in pure water and natural water. Limnol. Oceanogr. 11: 264-277.

Carritt, D.E. 1954. Atmospheric pressure changes and gas solubility. Deep-Sea Res. 2: 59-62.

Craig, H. 1969. Abyssal carbon and radiocarbon in the Pacific. J. Geophys. Res. 74: 5491-5506.

Craig, H., P.F. Weiss and W.B. Clarke. 1967. Dissolved gases in the Equatorial and South Pacific Ocean. J. Geophys. Res. 72: 6165-6181.

Douglas, E. 1964. Solubilities of oxygen, argon and nitrogen in distilled water. J. Phys. Chem. 68: 169-174.

Douglas, E. 1965. Solubilities of argon and nitrogen in sea water. J. Phys. Chem. 69: 2608-2610.

Green, E.J. and D.C. Carritt. 1967. New tables for oxygen saturation of sea water. J. Mar. Res. 25: 140-147.

Klots, C.E. and B.B. Benson. 1963. Solubilities of nitrogen, oxygen and argon in distilled water. J. Mar. Res. 21: 48-57.

Kroopnick, P. and H. Craig. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. Science 175: 54-55.

Menzel, D. and J. Ryther. 1968. Organic carbon and the oxygen minimum in the South Atlantic Ocean. Deep-Sea Res. 15: 327.

Murray, C.N. and J.P. Riley. 1969. The solubility of gases in distilled water and sea water. II. Oxygen. Deep-Sea Res. 16: 311-320.

Murray, C.N., J.P. Riley and T.R.S. Wilson. 1969. The solubility of gases in distilled water and sea water. I. Nitrogen. Deep-Sea Res. 16: 297-310.

Reeburgh, W.S. 1969. Observations of gases in Chesapeake Bay sediments. Limnol. Oceanogr. 14: 368-375.

Richards, F.A. 1957. Oxygen in the ocean. In: Chapter 9, Geol. Soc. America Memoir 67, Vol. 1, p. 185-238.

Seiler, W. and U. Schmidt. 1974. Dissolved nonconservative gases in seawater. p. 219-244. In: E.D. Goldberg (ed.), The Sea, v. 5. Wiley-Interscience.

Swinnerton, J.W., V.J. Linnebom, and R.A. Lamontagne. 1970. The ocean, a natural source of carbon monoxide. Science 67: 984.

Wyrtki, K. 1962. The oxygen minimum in relation to oceanic circulation. Deep-Sea Res. 9: 11-23.

b. *Analytical methods.*

Carpenter, J.H. 1965. The accuracy of the Winkler method for dissolved oxygen analysis. Limnol. Oceanogr. 10: 135-140.

Carpenter, J.H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr. 10: 141-143.

Carritt, D.E. and J.H. Carpenter. 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in sea water; a NASCO report. J. Mar. Res. 24: 286-318.

McKinney, R.E. and R.E. Conway. 1957. Chemical oxygen in biological waste treatment. Sewage and Industr. Wastes. 29: 1097-1106.

Scholander, P.L., L. van Dam, C.L. Claff, and J. Kanwisher. 1955. Microgasometric determination of dissolved oxygen and nitrogen. Biol. Bull. 109: 328-34.

Swinnerton, J.W., V.J. Linnebom and C.H. Cheek. 1968. A sensitive gas chromatographic method for determining carbon monoxide in sea water. Limnol. Oceanogr. 13: 193.

c. *Exchange across sea surface; equilibrium*

Atkinson, L.P. 1973. Effect of air bubble solution on air-sea exchange. J. Geophys. Res. 78: 962-968.

Craig, J. and L. Gordon. 1963. Nitrous oxide in the ocean and the marine atmosphere. Geochim. Cosmochim. Acta 27: 949.

Kanwisher, J. 1963. On the exchange of gases between the atmosphere and the sea. Deep-Sea Res. 10: 195-207.

Postma, H. 1964. The exchange of oxygen and carbon dioxide between the ocean and atmosphere. Netherlands J. Sea Res. 2: 258-283.

Redfield, A.C. 1948. The exchange of oxygen across the sea surface. J. Mar. Res. 7: 347-361.

Swinnerton, J.W., V.H. Linnebom, and R.A. Lamontagne. 1970. Distribution of carbon monoxide between the atmosphere and the ocean. Annals. New York Acad. Sciences 174: 96-101.

Swinnerton, J.W., V.J. Linnebom, and C.H. Cheek. 1969. Distribution of methane and carbon monoxide between the atmosphere and natural waters. Environ. Sci. Tech. 3: 836.

d. *Anoxic conditions and redox potential*

Breck, W.G. 1972. Redox potentials by equilibration. Jour. Mar. Res. 30: 121-139.

Breck, W.G. 1974. Redox levels in the sea. p. 153-180. In: E.D. Goldberg, (ed.), The Sea, v. 5. Wiley-Interscience.

Cooper, L.H.N. 1937. Oxidation-reduction potential in sea water. Jour. Mar. Biol. Ass. U.K. 22: 167-176.

Fanning, K.A. and M.E.G. Pilson. 1972. A model for the anoxic zone of the Cariaco Trench. Deep-Sea Res. 19: 847-864.

Gardner, L.R. 1973. Chemical models for sulfate reduction in closed anaerobic marine environments. Geochim. Cosmochim. Acta 37: 53-68.

Richards, F.A. and R.F. Vaccaro. 1956. The Cariaco Trench, an anaerobic basin in the Caribbean Sea. Deep-Sea Res. 3: 214-228.

Richards, F.A. and B.B. Benson. 1961. Nitrogen/argon and nitrogen isotope ratios in two anaerobic environments, the Cariaco Trench in the Caribbean Sea and Dramsfjord, Norway. Deep-Sea Res. 7: 254-264.

Richards, F.A. 1965. Chemical observations in some anoxic, sulfide-bearing basins and fjords, p. 215-243. In: Proc. Second Intern. Conf. Water Pollution Res., Tokyo, 1964, Pergamon, New York.

Richards, F.A., J.D. Cline, W.W. Broenkow and L.P. Atkinson. 1965. Some consequences of the decomposition of organic matter in Lake Nitinat, an anoxic fjord. Limnol. Oceanogr. Redfield Anniversary Vol. 10: R185-R201.

Stumm, W. 1966. Redox potential as an environmental parameter; conceptual significance and operational limitation: Third International Conf. on Water Pollution Research, Paper No. 13, pp. 1-16.

2. *Carbon dioxide*

a. *pH, alkalinity*

Anderson, D.H. and R.J. Robinson. 1946. Rapid electrometric determination of the alkalinity of sea water. Industrial and Engineering Chem. 18: 767-769.

Bates, R.G. 1954. Electrometric pH determinations. Wiley, New York.

Culberson, C.R., M. Pytkowicz, J.E. Hawley. 1970. Seawater alkalinity determination by the pH method. J. Mar. Res. 28: 15-21.

Edmond, J.M. 1970. High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration. Deep-Sea Res. 17: 737-750.

Feldman, I. 1965. Use and abuse of pH measurements. Anal. Chem. 28: 1859-1866.

Gassaway, J.D. 1957. New method for boron determination in sea water and some preliminary results. Int. J. Oceanol. Limnol. 1: 85-90.

Gast, J.A. and T.G. Thompson. 1959. Evaporation of boric acid from sea water. Tellus 11: 344-347.

Gast, J.A. and T.G. Thompson. 1958. Determination of the alkalinity and borate concentration of sea water. Anal. Chem. 30: 1549-1551.

Gieskes, J.M. 1974. The alkalinity-total carbon dioxide system in sea-waters. p. 123-152. In: E.D. Goldberg, (ed.), The Sea, v. 5. Wiley-Interscience.

Kester, D.R. and R.M. Pytkowicz. 1967. Determination of the apparent dissociation constants of phosphoric acid in seawater. Limnol. Oceanogr. 12: 243-252.

Koczy, F.F. 1956. The specific alkalinity. Deep-Sea Res. 3: 279.

Lyman, J. 1957. The buffer mechanism of sea water, Ph.D. Dissertation, UCLA, 196 pp.

Noakes, J.E. and D.W. Hood. 1961. Boron - boric acid complexes in sea water. Deep-Sea Res. 8: 121-129.

Park, K. 1963. Conductometric determination of alkalinity of sea water. Anal. Chem. 35: 1549-1550.

Pytkowicz, R.M., I.W. Duedall and B.C. Burgener. 1966. Reproducibility of pH measurements in seawater. Limnol. Oceanogr. 11: 417-419.

Rakestraw, N.W. 1949. The conception of alkalinity or excess base of sea water. J. Mar. Res. 8: 14-20.

Smith, W.H. and D.W. Hood. 1964. pH measurements in the ocean: a sea water secondary buffer system. p. 185-202. In: Y. Miyake and T. Koyame (eds.), Recent Researches in the Field... Geochemistry. Maruzen Company, Tokyo.

Wangersky, P.J. 1972. The control of seawater pH by ion pairing. Limnol. Oceanogr. 17: 1-6.

Williams, P.M. and P.M. Strack. 1966. Complexes of boric acid with organic cis-diols in sea water. Limnol. Oceanogr. 11: 401-403.

b. *Carbon dioxide - alkalinity relationships*

Dyrssen, D. and L.G. Sillen. 1967. Alkalinity and total carbonate in sea water: A plea for p-T-independent data. Tellus 19: 113-121.

Garrels, R.M., M.E. Thompson, and R. Siever. 1960. Stability of some carbonates at 25C and one atmosphere total pressure. Am. J. Sci. 258: 402-418.

Garrels, R.M., M.E. Thompson and R. Siever. 1961. Control of carbonate solubility by carbonate complexes. Am. J. Sci. 259: 24-45.

Garrels, R.M. and M.E. Thompson. 1962. A chemical model for seawater at 25C and one atmosphere total pressure. Am. J. Sci. 260: 57-66.

Kanwisher, J. 1960. pCO_2 in sea water and its effect on the movement of CO_2 in nature. Tellus 12: 209-215.

Keeling, C.D., N.W. Rakestraw and L.S. Waterman. 1965. Carbon dioxide in the surface waters of the Pacific Ocean. I. Measurements and distribution. J. Geophys. Res. 70: 6087-6098.

Keeling, C.D. 1968. Carbon dioxide in surface ocean waters, global distribution. J. Geophys. Res. 73: 4543-4553.

Kelley, J.J., Jr. 1968. Carbon dioxide in the seawater under the arctic ice. Nature 218: 862-864.

Kern, D.M. 1960. The hydration of carbon dioxide. J. Chem. Ed. 37: 14-23.

Li, Y.H., T. Takahashi, and W.S. Broecker. 1969. Degree of saturation of calcium carbonate in the oceans. J. Geophys. Res. 74: 5507.

Revelle, R. and R. Fairbridge. 1957. Carbonates and carbon dioxide. pp. 239-295. In: Treatise on marine ecology and paleoecology. Geol. Soc. Amer. Mem. 67.

Spencer, C.P. 1965. The carbon dioxide system in sea waters: A critical appraisal. Oceanogr. Mar. Biol. Ann. Reviews 3: 31-57.

Takahashi, T. R.F. Weiss, C.H. Culberson, J.M. Edmond, D.E. Hammond, C.S. Wong, Y.H. Li and A.E. Bainbridge. 1970. A carbonate chemistry profile at the 1969 GEOSECS intercalibration station in the Eastern Pacific Ocean. J. Geophys. Res. 75: 7648-7666.

Weber, W.J. and W. Stumm. 1963. Buffer systems of natural fresh waters. J. Chem. Eng. Data 8: 464-468.

c. *Analytical methods*

Ben-Yaakov, S. 1970. A method for calculating the in situ pH of seawater. Limnol. Oceanogr. 15: 326-328.

Edmond, J.M. 1970. High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration. Deep-Sea Res. 17: 737-750.

Edmond, J.M. and J.M. Gieskes. 1970. On the calculation of the degree of saturation of sea water with respect to calcium carbonate under in situ conditions. Geochim. Cosmochim. Acta 34: 1261-1291.

Hansson, I. 1973. A new set of acidity constants for carbonic acid and boric acid in sea water. Deep-Sea Res. 20: 461-478.

Hansson, I. 1973. A new set of pH scales and standard buffers for sea water. Deep-Sea Res. 20: 479-491.

Park, K. 1969. Oceanic CO_2 System: An evaluation of ten methods of investigation. Limnol. Oceanogr. 14: 179-186.

d. *Exchange between the sea and the atmosphere*

Bolin, B. 1960. On the exchange of carbon dioxide between the atmosphere and the sea. Tellus 12: 274-281.

Ibert, E.R. 1963. An investigation of the distribution of carbon dioxide between the atmosphere and the sea. Ph.D. Dissertation, Texas A&M University.

Kanwisher, J. 1963. Effect of wind on CO_2 exchange across the sea surface. J. Geophys. Res. 68: 3921-3927.

Keeling, C.D. 1965. Carbon dioxide in the surface waters of the Pacific Ocean, II. Calculations of exchange with the atmosphere. J. Geophys. Res. 70: 6099-6102.

Postma, H. 1964. The exchange of oxygen and carbon dioxide between the ocean and the atmosphere. Netherlands J. of Sea Res. 2: 258-283.

Revelle, R. and H.E. Suess. 1957. Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades. Tellus 2: 18-27.

Takahashi, T. 1961. Carbon dioxide in the atmosphere and Atlantic Ocean water. J. Geophys. Res. 66: 477-494.

Quinn, J.A. and N.C. Otto. 1971. Carbon dioxide exchange at the air-sea interface: Flux augmentation by chemical reaction. J. Geophys. Res. 76: 1539-1549.

e. *Carbonates*

Ames, L.L., Jr. 1959. The genesis of carbonate apatites. Econ. Geol. 54: 829-841.

Berner, R.A. 1968. Calcium carbonate concretions formed by the decomposition of organic matter. Science 159: 195-197.

Berner, R.A. and J.W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water. IV. Theory of calcite dissolution. Amer. J. Sci. 274: 108-134.

Chave, K.E. 1962. Factors influencing the mineralogy of carbonate sediments Limnol. Oceanogr. 7: 218-233.

Chave, K.E., K.S. Deffeyes, P.K. Weyl, R.M. Garrels and M.E. Thompson. 1962. Observations on the solubility of skeletal carbonates in aqueous solutions. Science 137: 33-34.

Chave, K.E. and R.F. Schmalz. 1966. Carbonate-seawater interactions. Geochim. Cosmochim. Acta 30: 1037-1048.

Chave, K.E. 1965. $CaCO_3$: Association of organic matter in surface seawater. Science 148: 1723-1724.

Chave, K.E. and E. Suess. 1970. Calcium carbonate saturation in seawater: Effects of dissolved organic matter. Limnol. Oceanogr. 15: 633-637.

LeGeros, R.Z. 1965. Effect of carbonate on the lattice parameters of apatite. Nature 206: 403-404.

LeGeros, R.Z., O.R. Trautz, J.P. LeGeros, and E. Klein. 1967. Apatite crystallites: Effect of carbonate on morphology. Science 155: 1409-1411.

LeGeros, R.S., O.R. Trautz, E. Klein and J.P. LeGeros. 1969. Two types of carbonate substitution in the apatite structure. Experimentia 24: 5-7.

Morse, J.W. and R.A. Berner. 1972. Dissolution kinetics of calcium carbonate in seawater: II. A kinetic origin of the lysocline. Am. Jour. Sci. 272: 840-851.

Morse, J.W. 1974. Dissolution kinetics of calcium carbonate in seawater. III. A new method for the study of carbonate reaction kinetics. Am. Jour. Sci. 274: 97-107.

Pytkowicz, R.M. 1965. Rates of inorganic calcium carbonate nucleation. J. Geol. 73: 196-199.

Pytkowicz, R.M. 1965. $CaCO_3$ saturation in the ocean. Limnol. Oceanogr. 10: 220-225.

Schmalz, R.F. and K.E. Chave. 1963. Calcium carbonate: Factors affecting saturation in ocean waters off Bermuda. Science 139: 1206-1207.

Simpson, D.R. 1967. Effect of pH and solution concentration on the composition of carbonate apatite. Am. Miner. 52: 896-902.

Weyl, P.K. 1961. The carbonate saturometer. J. Geol. 69: 32-44.

6. *World distribution of CO_2*

Andersen, N.R. and A. Malahoff. eds. 1977. Fate of Fossil Fuel CO_2. Plenum Press, New York.

Broecker W., Y-H. Li and T-H Peng. 1971. Carbon dioxide - man's unseen artifact. p. 287-324. In: D.W. Hood (ed), Impingement of Man on the Oceans. Wiley-Interscience.

F. *Geochemical Cycling*

Berner, R.A. 1974. Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus, and silicon in anoxic marine sediments. p. 427-450. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

Bogoyavlenskiy. 1966: Distribution and migration of dissolved silica in oceans. Internat. Geology Rev. 9: 133-153.

Calvert, S.E. 1968. Silica balance in the ocean and diagenesis. Nature 219: 919-920.

Drever, J.I. 1974. The magnesium problem. p. 337-358. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

Garlick, G.D. 1974. The stable isotopes of oxygen, carbon, and hydrogen in the marine environment. p. 393-426. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

Garrels, R.M. and E.A. Perry, Jr. 1974. Cycling of carbon, sulfur, and oxygen through geologic time. p. 303-336. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

Mackenzie, F.T. and R.M. Garrels. 1965. Silicates: Reactivity with sea water. Science 150: 57-58.

Mackenzie, F.T. and R.M. Garrels. 1967. Silica-bicarbonate balance in the ocean and early diagenesis. J. Sed. Petrol. 36: 1075-1084.

Mackenzie, F.T., R.M. Garrels, O.P. Bricker, and F. Bickley. 1967. Silica in sea water: Control by silicate minerals. Science 155: 1404-1405.

Perry, E.A., Jr. 1971. Silicate-seawater equilibria in the ocean system: Discussion. Deep-Sea Res. 18: 921-924.

Wollast, R. 1974. The silica problem. p. 359-392. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

G. *Nutrients*

1. *Nitrogen*

a. *Analytical methods*

Bendschneider, K. and R.J. Robinson. 1952. A new spectrophotometric method for determination of nitrite in sea water. J. Mar. Res. 11: 87-96.

Morris, A.W., and J.P. Riley. 1963. The determination of nitrate in sea water. Anal. Chim. Acta 29: 272-279.

Newell, B.S. 1967. Determination of ammonia in sea water. J. Mar. Biol. Assn. U.K. 47: 271-80.

Wood, E.D., F.A. J. Armstrong, and F.A. Richards. 1967. Determination of nitrate in sea water by cadmium-copper reduction to nitrite. J.Mar. Biol. Assn. U.K. 47: 23-31.

b. *Variation and distribution of nitrogen in the sea.*

Broenkow, W.W. 1965. The distribution of nutrients in the Costa Rico Dome in the eastern topical Pacific Ocean. Limnol. Oceanogr. 10: 40-52.

Degens, E.T. 1970. Molecular nature of nitrogenous compounds in sea water and recent marine sediments, p. 77 to 106. In D.W. Hood (ed.), Organic Matter in Natural Waters. Occ. Pub. No. 1, Institute of Marine Science, Univ. Alaska, College, Alaska.

Dugdale, R.C. 1967. Nutrient limitation in the sea: Dynamics, identification and significance. Limnol. Oceanogr. 12: 685-695.

Grill, E.V. and F.A. Richards. 1964. Nutrient regeneration from phytoplankton decomposing in seawater. J. Mar. Res. 22: 51-69.

Johannes, R.E. 1968. Nutrient regeneration in lakes and oceans. In: M.R. Droop and E.J.F. Wood (eds.), Advances in Microbiology of the Sea, Vol. 1. Academic.

Junge, C. and J. Hahn. 1971. N_2O measurements in the North Atlantic. J. Geophys. Res. 76: 8143-8146.

Menzel, D. and J. Spaeth. 1962. Occurrence of ammonia in Sargasso Sea Water and in rain water at Bermuda. Limnol. Oceanogr. 7: 159-162.

Ryther, J.H. and W.M. Dunstan. 1971. Nitrogen, phosphorous, and eutrophication in the coastal marine environment. Science 171: 1008-1013.

Stefansson, U. and F.A. Richards. 1963. Processes contributing to the nutrient distributions off the Columbia River and Strait of San Juan de Fuca. Limnol. Oceanogr. 8: 394-410.

Stefansson, U. 1966. Influence of the Surtsey eruption on the nutrient content of the surrounding seawater. J. Mar. Res. 24: 241-268.

Stefansson, U. 1968. Nitrate-phosphate relationships in the Irminger Sea. J. Cons. perm. int. Explor. Mer. 32: 118-200.

Tsunogai, S. 1971. Ammonia in the oceanic atmoshpere and the cycle of nitrogen compounds through the atmosphere and the hydrosphere. Geochem. Jour. 5: 57-67.

Walsh, J.J. and D.H. Cushing. 1976. Ecology of the Seas. Saunders.

Walsh, J.J. and R.C. Dugdale. 1972. Nutrient submodels and simulation models of phytoplankton production in the sea. p. 171-191. In: H.E. Allen and J.R. Kramer (eds.), Nutrients in Natural Waters. Wiley.

2. *Phosphorus*

a. *Analytical methods*

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27: 31-36.

b. *Variations and distribution of phosphorous in the sea.*

Baylor, E.R., W.H. Sutcliffe, and D.S. Hirschfeld. 1962. Adsorption of phosphates onto bubbles. Deep-Sea Res. 9: 120.

D'Anglejan, B.F. 1968. Phosphate diagenesis of carbonate sediments as a mode of in situ formation of marine phosphorites: Observations in a core from the eastern Pacific. Can. Jour. Earth Sci. 5: 81-87.

Harrison, M.J., R.E. Pacha, and R.Y. Morita. 1972. Solubilization of inorganic phosphates by bacteria isolated from upper Klamath Lake sediment. Limnol. Oceanogr. 17: 50-57.

Malone, P.G. and K.M. Towe. 1970. Microbial carbonate and phosphate precipitates from sea water cultures. Mar. Geol. 9: 120.

Obihara, C.H. and E.W. Russel. 1972. Specific adsorption of silicate and phosphate by soils. J. Soil Sci. 23: 105-117.

Otsuki, A. and R.G. Wetzel. 1972. Coprecipitation of phosphate with carbonates in a marl lake. Limnol. Oceanogr. 17: 763-767.

Pomeroy, L.R., E.E. Smith, and C.M. Grant. 1965. The exchange of phosphate between estuarine water and sediments. Limnol. Oceanogr. 10: 167-172.

Redfield, A.C. 1942. The processes determing the concentration of oxygen, phosphate, and other organic derivatives. Papers in Physical Oceanography and Meterology, M.I.T. and Woods Hole Oceanographic Inst. IX (2), 1-22.

Rittenberg, S.C., K.O. Emery, and W.D. Orr. 1955. Regeneration of nutrients in sediments of marine basins. Deep-Sea Res. 3: 23-45.

Serruya, C. 1971. Lake Kinneret: The nutrient chemistry of the sediments. Limnol. Oceanogr. 16: 510-521.

Simkiss, K. 1964. Phosphates as crystal poisons of calcification. Biol. Rev. 39: 487-505.

Simpson, D.R., 1966. Apatite and octo-calcium phosphate: effects of carbon dioxide and halogens on formation. Science 154: 1660-1661.

Stumm, W. and J.O. Leckie. 1970. Phosphate exchange with sediments: Its role in the productivity of surface waters. In: Adv. in Water Pollution Research, 2. Pergamon Press, New York, III, 26/1-26/16.

Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1970. Adsorption and desorption of inorganic phosphorus by lake sediments in a 0.1 M NaCl system. Envir. Sci. Technol. 4: 517-519.

Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong. 1971. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Envir. Sci. Technol. 5: 1113-1120.

3. *Silicon*

*a. *Sources and silica mass balance*

Kellogg, W.W., R.D. Cadle, E.R. Allen, A.L. Lazrus, and E.A. Martell. 1972. The sulfur cycle. Science 175: 587-596.

Mackenzie, F.T. and R.M. Garrels. 1965. Silicates: Reactivity with sea water. Science 150: 57-58.

Mackenzie, F.T. 1966. Chemical mass balance between rivers and oceans. Am. J. Sci. 264: 507-525.

Mackenzie, F.T., R.M. Garrels, O.P. Bricker, and F. Bickley. 1967. Silica in sea water: Control by silicate minerals. Science 155: 1404-1405.

b. *Analytical methods*

Mullin, J.B. and J.P. Riley. 1955. The colorimetric determination of silicate with special reference to sea and natural waters. Anal. Chim. Acta. 12: 162-176.

c. *Biological importance*

Berger, W.H. 1968. Radiolarian skeletons: Solution at depths. Science 159: 1237-1238.

d. *Distribution of silicon in the sea*

Stefansson, U. and L.P. Atkinson. 1971. Relationship of potential temperature and silicate in the deep waters between Cape Lookout, N.C. and Bermuda. J. Mar. Res. 29: 306-318.

H. *Organic Matter in the Sea*

1. *Dissolved organic matter*

a. *Origin and fate*

Andersen, N.R., ed. 1977. Concepts in Marine Organic Chemistry. Mar. Chem. 5 (in press).

Armstrong, F.A.J., P.M. Williams, and J.D.H. Strickland. 1966. Photo-oxidation of organic matter in sea water by ultraviolet radiation, analytical and other applications. Nature 211: 481-3.

Armstrong, F.A.J. and S. Tibbits. 1968. Photochemical combustion of organic matter in sea water for nitrogen, phosphorous and carbon determination. J. Mar. Biol. Assoc. U.K. 48: 143-152.

Richards, F.A., J.D. Cline, W.W. Broenkow and L.P. Atkinson. 1965. Some consequences of the decomposition of organic matter in Lake Nitinat, an anoxic fjord. Limnol. Oceanogr. Redfield Anniversary Vol. 10: R185-R201.

Thayer, L.A. 1931. Bacterial genesis of hydrocarbons from fatty acids. Am. Assoc. Bull. 15: 441-453.

Wilson, D.F., J.W. Swinnerton, and R.A. Lamontagne. 1970. Production of CO and gaseous hydrocarbons in seawater; relation to dissolved organic carbon. Science 168: 1577.

b. *Distributions and complications*

Kalle, K. 1966. The problem of the Gelbstoff in the sea. Oceanogr. Mar. Biol. Ann. Rev. 4: 91-104.

Linnenbom, V.J. and J.W. Swinnerton. 1970. Low molecular weight hydrocarbons and carbon monoxide in sea water, p. 455-467. In: D.W. Hood, (ed.), Organic Matter in Natural Waters, Occ. Publ. No. 1, Institute of Marine Science, Univ. Alaska College, Alaska.

Menzel, D.W. and J.J. Goering. 1966. The distribution of organic detritus in the ocean. Limnol. Oceanogr. 11: 333-337.

Sharp, J.H. 1973. Size classes of organic carbon in seawater. Limnol. Oceanogr. 18: 441-447.

Thorstensen, D.C. 1970. Equilibrium distribution of small organic molecules in natural waters. Geochim. Cosmochim. Acta 34: 745-770.

Williams, P.J. le B. 1975. Biological and chemical aspects of dissolved organic material in seawater. p. 301-364. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 2. Academic.

Williams, P.M. 1971. The distribution and cycling of organic matter in the ocean. p. 145-161. In: S.J. Faust and J.V. Hunter (eds.), Organic Compounds in Aquatic Environments. Marcel Dekker.

2. *Particulate organic matter*

a. *Origin and composition*

Menzel, D. and J. Ryther. 1964. The composition of particulate organic matter in the Western North Atlantic. Limnol. Oceanogr. 9: 179-186.

Riley, G.A. 1970. Particulate organic matter in the sea. Adv. Mar. Biol. 8: 1-118.

Parsons, T.R. 1975. Particulate organic carbon in the ocean. p. 365-385, In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 2. Academic.

Vallentyne, J.R. 1962. Solubility and the decomposition of organic matter in nature. Arch. Hydrobiol. 58: 423-434.

Wangersky, P.J. 1965. The organic chemistry of sea water. Amer. Scientist 53: 358-374.

Williams, P.M. and L.I. Gordon. 1969. Carbon 13, Carbon 12 ratios in dissolved and particulate organic matter in the sea. University of California, Institute of Marine Resources, Selected Papers.

b. *Surface films*

Baier, R.E. 1972. Organic films on neutral waters: Their retrieval identification, and modes of elemination. J. Geophys. Res. 77: 5062.

Garrett, W.D. 1965. Collection of slick-forming materials from the sea surface. Limnol. Oceanogr. 10: 602-605.

Garrett, W.D. 1967. The organic chemical composition of the ocean surface. Deep-Sea Res. 14: 221-227.

Garrett, W.D. 1968. The influence of monomolecular surface films on the production of condensation nuclei from bubbled sea water. J. Geophys. Res. 73: 5145.

Harvey, G.W. 1966. Microlayer collection from the sea surface: A new method and initial results. Limnol. Oceanogr. 11: 608-613.

Jarvis, N.L. 1962. The effect of monomolecular films on surface temperature and convective motion at the water/air interface. J. of Colloid Sci. 17: 512-522.

Jarvis, N.L. 1967. Adsorption of surface material at the sea-air interface. Limnol. Oceanogr. 12: 213-221.

Jarvis, N.L., W.D. Garrett, M.A. Scheiman, and C.O. Timmons. 1967. Surface chemical characterization of surface active material in sea water. Limnol. Oceanogr. 12: 88-97.

Lafond, E.C. 1959. Slicks and temperature structure in the sea. NEL/ Report. 937: 1-35.

Williams, P.M. 1967. Sea surface chemistry: Organic carbon and organic and inorganic nitrogen and phosphorus in surface film and subsurface waters. Deep-Sea Res. 14: 791-800.

3. *Biological effects on seawater chemistry*

Holm-Hansen, O., J.D.H. Strickland and P.M. Williams. 1966. A detailed analysis of biologically important substances in a profile off Southern California. Limnol. Oceanogr. 11: 548-561.

Redfield, A.C. 1958. The biological control of chemical factors in the environment. Amer. Scientist 46: 205-221.

Redfield, A.C., B. Ketchum and F.A. Richards. 1963. The influence of organisms on the composition of sea-water, p. 26-77. In: M.N. Hill (ed.), The Sea, v. 2, Wiley-Interscience.

Riley, G.A. 1965. A mathematical model of regional variations in plankton. Limnol. Oceanogr. Redfield Anniversary Vol. 10:R202-R215.

I. *Marine Sediments*

Anikouchine, W.A. 1967. Dissolved chemical substances in compacting marine sediments. J. Geophys. Res. 72: 505-509.

Bader, R.G. 1955. Carbon and nitrogen relations in surface and subsurface marine sediments. Geochim. Cosmochim. Acta 7: 205-211.

Berner, R.A. 1969. Migration of iron and sulfur within anaerobic sediments during early diagenesis. Am. Jour. Sci. 267: 19-42.

Berner, R.A. 1974. Kinetic models for the early diagenesis of nitrogen, phosphorus and silicon in anoxic marine sediments, p. 427-450. In: E.D. Goldberg (ed.), The Sea, V.5. Wiley-Interscience.

Bonatti, E., D.E. Fisher, O. Joensuu, and H.S. Rydell. 1971. Postdepositional mobility of some transition elements, phosphorous, uranium and thorium in deep sea sediments. Geochim. Cosmochim. Acta 35: 189.

Brooks, R.R., B.J. Presley, and I.R. Kaplan. 1968. Trace elements in the interstitial waters of marine sediments. Geochim. Cosmochim. Acta 32: 397-414.

Brown, F.A., M.J. Baedecker, A. Nissenbaum, and I.R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - III. Changes in organic constitutents of sediment. Geochim. Cosmochim. Acta 36: 1185-1203.

Calvert, S.E. and N.B. Price. 1972. Diffusion and reaction profiles in the pore waters of marine sediments. Earth Planet. Sci. Lett. 16: 245-249.

Chow, T., K. Bruland, K. Bertine, A. Soutar, M. Koide and E. Goldberg. 1973. Lead pollution: Records in southern California coastal sediments. Science 181: 551-552.

Cronan, D.S. 1974. Authigenic minerals in deep-sea sediments. p. 491-526. In: E.D. Goldberg (ed.), The Sea, V.5. Wiley-Interscience.

Duursma, E.K. 1966. Moecular diffusion of radioisotopes in interstitial waters of sediments. Symposium on the disposal of radioactive wastes into seas, oceans and surface waters. IAEA., Vienna, 16-20 May 1966.

Fanning, K.A. and M.E.Q. Pilson. 1971. Interstitial silica and pH in marine sediments: Some effects of sampling procedures. 173: 1228-1231.

Friedman, G.M., B.F. Fabricand, E.S. Imbimbo, M.E. Brey and J.E. Sanders. 1968. Chemical changes in interstitial waters from continental shelf sediments. Jour. Sed. Pet. 38: 1313-1319.

Goldberg, E.D. and K. Bruland. 1974. Radioactive geochronologies. p. 451-490. In: E.D. Goldberg (ed.), The Sea, V.5. Wiley-Interscience.

Gulbrandsen, R.A. 1969. Physical and chemical factors in the formation of marine apatite. Econ. Geol. 64: 365-382.

Jones, A.S.G. 1972. A partial geochemical study of shallow marine sediments, Cardigan Bay (Wales). Mar. Geol. 12: 313-333.

Kaplan, I.R., K.O. Emery, and S.C. Rittenberg. 1963. The distribution and isotopic abundance of sulfur in recent marine sediments off southern California. Geochim. Cosmochim. Acta 27: 297-331.

Kaplan, I.R. and S.C. Rittenberg. 1963. Basin sedimentation and diagenesis, p. 583-619. In: M.N. Hill (ed.), The Sea, V.3. Wiley-Interscience.

Krauskopf, K.B. 1975. Separation of manganese from iron in sedimentary processes. Geochim. Cosmochim. Acta 12: p. 61-84.

Manheim, F.T. 1974. Comparative studies of extraction of sediment interslitial waters: Discussion and comment on the current state of interstitial water studies. Clays Clay Min. 22: 337-343.

Manheim, F.T. and F.L. Sayles. 1974. Composition and origin of interstitial waters of marine sediments, based on deep-sea drill cores. p. 527-568. In: E.D. Goldberg (ed.), The Sea, V.5. Wiley-Interscience.

Martins, C.S. and R.C. Harriss. 1970. Inhibition of apatite precipitation in the marine environment by magnesium ions. Geochim. Cosmochim. Acta 34: 621-625.

Murthy, A.S. Parshiva and R.E. Ferrell, Jr. 1972. Comparative chemical compositon of sediment interstitial waters. Clays Clay Min. 20: 317-321.

Nissenbaum, A., B.J. Presley, and I.R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - I. Chemical and isotopic changes in major components of interstitial water. Geochim. Cosmochim. Acta 36: 1007-1027.

Nriagu, J.O. 1972. Stability of vivanite and ion-pair formation in the System $Fe_3(PO_4)_2$ - H_3PO_4 - H_2O. Geochim. Cosmochim. Acta 36: 459-470.

Presley, B.J., R.R. Brooks, and I.R. Kaplan. 1967. Manganese and related elements in the interstitial water of marine sediments. Science 158: 906-909.

Presley, B.J. and I.R. Kaplan. 1968. Changes in dissolved sulfate, calcium and carbonate from interstitial water of near-shore sediments. Geochim. Cosmochim. Acta 32: 1037-1049.

Shapiro, J., W.T. Edmondson, and D.E. Allison. 1971. Changes in the chemical composition of sediments of Lake Washington, 1958-1970. Limnol. Oceanogr. 16: 437-452.

Strakhov, N.M. 1972. The balance of reducing processes in the sediments of the Pacific Ocean. Geological Institute, Academy of Sciences of the USSR, Moskow p. 65-92.

Wickman, F.E. 1954. The "total" amount of sediments and the composition of the "average igneous rock". Geochim. Cosmochim. Acta 5: 97-110.

Yen, T.F., ed. 1977. Chemistry of Marine Sediments. Ann Arbor Science. Ann Arbor, Michigan.

J. *Chemical Models of the Oceans*

Bolin, B. and H. Stommel. 1961. On the abyssal circulation of the world ocean. IV: Origin and rate of circulation of deep ocean water as determined with the aid of tracers. Deep-Sea Res. 8: 95-110.

Keeling, C.D. and B. Bolin. 1967. The simultaneous use of chemical tracers in oceanic studies. I. General theory of reservoir models. Tellus 19: 566-581.

Keeling, C.D. and B. Bolin. 1968. The simultaneous use of chemical tracers in oceanic studies. II. A three reservoir model of the North and South Pacific Oceans. Tellus 20: 17-54.

K. *Minor Elements and Trace Metals*

Barker, D.R. and H. Zeitlin. 1972. Metal-ion concentrations in sea-surface micro-layer and size-separated atmospheric aerosol samples in Hawaii. J. Geophys. Res. 77: 5076.

Barnes, S.S. and J. Dymond. 1967. Rate of accumulation of ferromanganese modules. Nature 218: 1218-1219.

Bradford, W.L. 1973. The determinations of stability constant for the aqueous complex $Zn(OH_2)^\circ$ using anodic stripping voltammetry. Limnol. Oceanogr. 18: 757-762.

Brewer, P.G. 1974. Minor elements in sea water, p. 415-497. In: J.P. Riley, and G. Skirrow (eds.), Chemical Oceanography, 2nd ed. v.1. Academic.

Cheney, E.S. and L.D. Vredenburgh. 1968. The role of iron sulfides in the diagenetic formation of iron-poor manganese modules. Jour. Sed. Pet. 38: 1363-1365.

Doyle, R.W. 1967. Eh and thermodynamic equilibrium in environments containing dissolved ferrous ion. Ph.D. Dissertation, Yale Univ.

Duce, R.A., J.G. Quinn, C.E. Olner, S.R. Piotrowicz, B.J. Ray, and T.L. Wade. 1972. Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. Science 176: 161-163.

Elderfield, H. 1970. Chromium speciation in sea water. Earth Planet. Sci. Lett. 9: 10-16.

Hood, D.W. 1967. Chemistry of the oceans: Some trace metal-organic associations and chemical parameter differences in top one meter of surface. Environ. Science Technol. 1: 303-305.

Kamp-Nielsen, L. 1972. Some comments on the determination of copper fractions in natural waters. Deep-Sea Res. 19: 899-902.

Piotrowicz, S.R., B.J. Ray, G.L. Hoffman, and R.A. Duce. Trace metal enrichment in the sea-surface microlayer. J. Geophys. Res. 77: 5243.

Spencer, D.W. and P.G. Brewer. 1971. Vertical advection diffusion and redox potentials as controls on the distribution of maganese and other trace metals dissolved in waters of the Black Sea. J. Geophys. Res. 76: 5877-5892.

Zirino, A. and M.L. Healy. 1970. Inorganic zinc complexes in seawater. Limnol. Oceanogr. 15: 956-958.

Zirino, A. and S. Yamamoto. 1972. A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. Limnol. Oceanogr. 17: 661-671.

L. *Radioisotopes and Stable Isotopes*

Broecker, W. 1963. Radioisotopes and large-scale oceanic mixing. In: M.N. Hill (ed.), The Sea, Vol. 2. Wiley-Interscience.

Burton, J.D. 1975. Radioactive nuclides in the marine environment, p. 91-192. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed. v. 1. Academic.

Craig, H. 1969. Abyssal carbon and radiocarbon in the Pacific. J. Geophys. Res. 74: 5491-5506.

Kemp, A.L.W. and H.G. Thode. 1968. The mechanism of the bacterial reduction of sulphate and of sulphite from isotope fractionation studies. Geochim. Cosmochim. Acta 32: 71-91.

Rees, C.E. 1973. A steady-state model for sulphur isotope fractionation in bacterial reduction processes. Geochim. Cosmochim. Acta 37: 1141-1162.

Preston, A. 1974. Artificial radioactivity in the sea. p. 817-836. In: E.D. Goldberg (ed.), The Sea, V.5. Wiley-Interscience.

Trudinger, P.A. and L.A. Chambers. 1973. Reversibility of bacterial sulfate reduction and its relevance to isotope fractionation. Geochim. Cosmochim. Acta 37: 1775-1778.

M. *Pollution of the Sea*

Carpenter, E.J., S.J. Anderson, G.R. Harvey, H.P. Miklas and B.B. Peck. 1972. Polystyrene spherules in coastal waters. Science 178: 749-750.

Church, T.M., ed. 1975. Marine Chemistry in the Coastal Environment. ACS Symposium Series 18.

Garrett, W.D. 1972. Impact of petroleum spills on the chemical and physical properties of the air/sea interface. NRL Report 7372, Naval Research Laboratory: 1-18.

Goldberg, E.D. 1975. Marine Pollution. p. 39-90 In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd ed., v. 3. Academic.

IDOE Baseline Conference, Baseline Studies of Pollutants in the Marine Environment and Research Recommendations.

Jernelov, A. 1974. Heavy metals, metalloids, and synthetic organics. p. 799-816. In: E.D. Goldberg (ed.), The Sea, V. 5. Wiley-Interscience.

Morris, B.F. 1971. Petroleum: Tar quantities floating in the northwestern Atlantic taken with a new quantitative neuston net. Science 173: 430-432.

National Academy of Sciences. 1975. Assessing potential ocean pollutants. National Research Council, Ocean Affairs Board. NAS, Washington, D.C.

National Academy of Sciences. 1976. Disposal in the marine environment: an oceanographic assessment. National Research Council, Ocean Affairs Board, NAS, Washington, D.C., 76 pp.

Seba, D.A. and E.F. Corcoran. 1969. Surface slicks as concentrators of pesticides in the marine environment. Pesticides Monitoring J. 3: 190-193.

Vernberg, F.J. and W.B. Vernberg, eds. 1974. Pollution and physiology of marine organisms. Academic.

Windom, H.L. and R.A. Duce, eds. 1976. Marine Pollutant Transfer. Lexington Books, Lexington, Mass.